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Issued October, 1893.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

ON APPARATUS FOR PROMOTING THE INTERACTION OF LIQUIDS AND GASES.[1]

BY PROFESSOR GEORGE LUNGE, PH.D., OF ZURICH.

BOTH in theoretical and industrial chemistry one of the most frequent operations consists in the interaction between liquids and gases. On the laboratory scale this operation presents but few difficulties and is generally treated rather briefly, both in chemical literature and in laboratory teaching. Even here the matter is not quite so plain as is assumed by many chemists, and the success or failure of analytical operations is sometimes intimately connected with this question. Where the task is merely that of treating a liquid with a gas, irrespective of the quantity of the latter consumed, the question is certainly simple enough. But where it is required to completely absorb every trace of a special gas diluted with a large quantity of inert gases, the ordinary wash bottles and similar apparatus are mostly insufficient. I have made this matter a special study in connection with the estimation of nitric oxide in chamber-exit gases and similar difficult cases, and I have described the best shape of absorbing apparatus for such purposes in a communication to the *Zeitschrift für Angewandte Chemie*, *1891*, p. 567, and in the *Journal of the Society of Chemical Industry*, *1890*, p. 1015.

The task becomes far more serious when operations on the

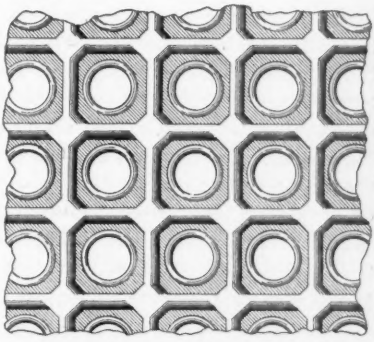
[1] Read before the World's Congress of Chemists, August 26, 1893.

large scale are concerned. The principal difficulties encountered here are the following: The immense volumes of gases which generally have to be dealt with and which sometimes contain but a small fraction of the gas or vapor which it is essential to bring into reaction with the liquid, and the necessity generally existing of employing the least possible quantity of liquid and of obtaining a strong solution, at the same time depriving the gases as completely as possible of the active constitutent in question. Special difficulties arise in many cases through the corrosive action of either the gases, or the absorbing liquid, or both; from the fact of tar, soot, flue dust, and other matters obstructing the channels through which the gas and the liquid have to pass; through the pasty condition of some absorbing media, such as Weldon mud, and in other ways. A whole book might be written on the construction of absorbing apparatus for all these cases, and if all the patents taken out in this line were to be noticed and illustrated therein such a book would be of formidable dimensions.

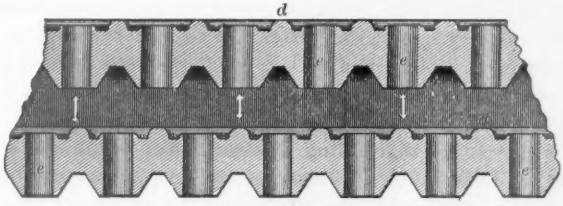
Certain points have always been taken for granted in devising apparatus of the class we are now speaking of. Everybody has tacitly assumed that the efficiency of such apparatus will be in proportion to the surface of contact and to the time which is given for the action. Dr. Hurter has attempted to give a scientific theory of that subject in several communications published in the *Journal of the Society of Chemical Industry*, *1885*, 639; *1887*, 707; *1893*, 226. Unfortunately the various conditions to be taken into account are too complicated and partly too little known to be amenable to scientific treatment, and if such a treatment is attempted after all, it may sometimes end in a decided failure and lead to entirely erroneous conclusions, as I have shown in my criticism of Dr. Hurter's last paper (the same journal, *1893*, 417). I shall not detain you here with a repetition of that criticism, but I shall straightway come to that apparatus for effecting contact between gases and liquids which I have devised myself and which has been carried out by Mr. Rohrmann, my co-patentee, in a manner acknowledged on all sides (quite prominently so by Dr. Hurter himself) as being a hitherto unparalleled achievement in chemical pottery.

I believe I may assume that my apparatus, which I have styled "plate column" or "plate tower," is already known to many of my hearers both from my own publications and from the trouble my friend, Mr. H. J. Davis, has taken to bring it before the American public. It is also described in the second edition of my "Sulphuric Acid and Alkali," at least so far as it is used in the manufacture of sulphuric acid, and I must refer to this for a detailed treatment of the subject. I will, therefore, only say a few words about it and illustrate these by a diagram and by a small specimen of the plates.

In order to adapt my apparatus to every kind of chemicals, the apparatus is made of a description of stoneware, absolutely resisting any chemical action of the strongest acids or alkaline liquids at temperatures far above 100° C., being at the same time very little sensitive to sudden changes of temperature up to the same limit. From



Plan of Lunge-Rohrmann Plate.



Section of Lunge-Rohrmann Plate.

this material my "plates" are manufactured on the following plan: Each plate is covered with a net work of ledges, about an eighth to a twelfth of an inch high, forming square basins of three-fourths of an inch square each, or less than that, according to the size of the holes, so that a plate of two by two feet contains from 800 to 1,200 of

such tiny basins. Each of these is provided with a central hole differing in width from less than a quarter to half an inch, according to circumstances. The top of each hole is surrounded by a slightly raised margin about a sixteenth of an inch deep. The plates are made on two different patterns, in one of which the basins are distant from the edge by half the width of a basin, whilst in the other pattern they come right up to the edge. Consequently when these two patterns of plates are superposed over one another, the holes in each plate correspond to the center of the cross formed by the ledges of the four basins just above and below. Hence when a liquid is run upon the plates each of the tiny basins is filled independently up to the edge of the margins round the holes. It then overflows through the hole and the drop thus formed falls upon the cross of ledges underneath, and is scattered over the four corresponding basins. Furrows on the bottom sides of the plates prevent the drops from running along the bottom and falling down in other places than those where they are intended to get to. While in this manner the liquid is spread on each plate in a thin film, which is constantly renewed by drops from above in the most regular manner, the gases are just as regularly divided, and issue in about 1000 jets through each plate without the possibility of any false channels being formed which so frequently occur in coke towers. As the gas jets ascend through the holes in any one of the plates, they strike against the solid portions of the plate next above, and are thus deflected from their course and constantly mixed over again. All this will be more completely understood by looking at the diagram.

It is easy to see that ordinary pottery, even of the best known makes, will not stand in this case. The plates must be very thin and at the same time they must be absolutely level and true in all parts. They must also bear a certain mechanical strain and sudden changes of temperature together with complete resistance to the action of chemicals. I did not know of any chemical pottery in Europe which fulfilled these conditions as well as that of Mr. Rohrmann, and for that reason I associated myself with him in that matter. I am glad to say that the large specimens of his plates submitted to the London and

Liverpool meetings of the Society of Chemical Industry by buyers of the same have excited universal admiration there.

Where no metal, not even lead, can be tolerated, the plates are made of circular shape and are built up with stoneware rings to keep them in proper distance, in stoneware pipes, thus forming columns of circular section and containing up to forty plates or even more. The sectional area of these columns is limited by the practicable width of the stoneware pipes and does not generally exceed two feet six inches. Large streams of gases, for which such a section would not suffice, have to be sub-divided among two or more columns. Where, however, lead is not excluded, the plates are made square, and are combined by means of specially designed bearers in such manner that any sectional area can be produced, the whole being enclosed in a leaden shell. The bearers support each plate independently of the others, and cover the whole of the lead so as to protect it entirely against the action of the heat and even of the chemicals, so that this system might be employed even in such cases where unprotected lead could not be employed.

Plate towers of these two constructions have now been proved to be, size for size, probably the most efficient apparatus hitherto invented for bringing gases into intimate contact with liquids, except in such cases where there is some solid or tarry matter present which would obstruct the holes and fill up the small basins. In all other cases the plate towers are from ten to twenty times as efficient as an equal space of the best arranged coke towers; and when they are compared with empty spaces, such as vitriol chambers, their efficiency is found to be hundreds of times greater than that of those spaces. From the nature of the case, plate towers can not be made of cheap materials turned out at a low price, but they are after all far cheaper than other apparatus with which they enter into competition, and would be so, even if their initial cost were equal to that of the coke towers or vitriol chambers they replace, seeing that they require next to no space, foundations and buildings, and that there is no pumping of liquids to a great height.

I now beg permission to illustrate my assertions by a number of examples taken from practical cases. I shall not touch upon

some applications which may ultimately become very important indeed, such as the manufacture of acetic acid, but I shall confine my remarks exclusively to the application of plate towers in the manufacture of the so-called heavy chemicals, that is, sulphuric, hydrochloric, nitric acid, and chlorine.

The application of the plate towers in the manufacture of sulphuric acid takes place in three different ways, as a partial substitute for the Glover towers, as a partial or entire equivalent of the Gay Lussac tower, and as a partial substitute for the vitriol chambers themselves, enabling a set of chambers to produce up to sixty or seventy per cent. more acid than without the plate towers. I shall quote practical instances for all three applications.

As far as the Glover tower is concerned, it stands to reason that it can not be entirely replaced by a plate column, and that for two reasons. In the first instance, the quantity of dust carried over from the pyrites, or even sulphur burners, is so great that the plates at the bottom of the tower would soon be choked up. Secondly, the temperature of the gases entering at the bottom and that of the acid descending in the tower is too different to expect any kind of pottery to stand the inevitable sudden changes and inequalities, at least in ordinary cases. Where, however, both these objections are done away with by a previous utilization of the burner gases for concentrating acid in lead or platinum dishes, as in Henry Glover's plan ("Sulphuric Acid and Alkali," second edition, **1**, p. 201), the whole Glover tower might be made of a plate column. In the ordinary towers, however, the bottom part will have to be packed in the usual way with a network of bricks, or flints, or cylinders, while the upper part is filled with my plates. Or else the same plan may be adopted which has been applied with full success by Dr. Petri at the Buchsweiler works in Alsace. There they burn spent gas oxide containing, besides free sulphur, some ammonia salts, part of which is not removed by washing and exerts a destructive influence in the niter in the Glover tower. This well-known reaction by which the nitrogen of both the ammonia and the nitrous vitriol is set free as such, takes place only at high temperatures. Reasoning from

this, Dr. Petri put on the top of his ordinary Glover tower a small plate column, consisting of thirteen layers of two plates each. The gases issuing from the Glover tower enter this small column at a temperature of 90° and leave it at 60° C., while the fresh nitrous vitriol is run in at the top and runs away at the bottom in order to feed the Glover tower. In this small column, holding altogether forty cubic feet, eighty per cent. of the denitration takes place, for which an ordinary Glover tower of eight by eight by twenty-five feet, equal to 1,600 cubic feet, is generally provided, leaving only twenty per cent. of the denitration to the Glover tower and effecting the denitration at such a low temperature that the ammonia exercises no injurious action. The contrast between the efficiency of those forty cubic feet of plate tower and the 1,600 cubic feet of ordinary Glover tower space is certainly startling. If, by the way, some of the plates should crack, they would all the same remain in their places and perform their work nearly as well as before.

The action of the plate column as a Gay Lussac tower is illustrated by an American works where a set of chambers of 212,000 cubic feet is provided with a plate tower of twenty layers of ten plates each. This tower, possessing about 280 cubic feet of active space, now fulfills the function of a coke tower of about 4,000 cubic feet. But it is evidently too wide for its present work, and hence requires too much acid for feeding it equally all over. It is hence intended to pass the gases from another set of 123,000 cubic feet through it and it is expected that it will be equal to this as well, in which case it would act like about 7,000 cubic feet of ordinary coke-tower space, that is, twenty-five times its cubic capacity.

A very important advantage of the plate tower over the ordinary coke tower is the chemical indifference of the former to all the gases concerned, whereas the coke, as I have repeatedly proved, acts as a reducing agent upon the nitrous compounds and causes a loss of niter together with a gradual crumbling of the coke packing, while a plate tower lasts practically forever.

Another advantage of the plate column is its inconsiderable height, which not merely makes the pumping of the absorbing

liquid much easier than with the ordinary coke tower, but in some cases admits of altogether dispensing with pumping. Thus, at the last-mentioned works the nitrous vitriol runs from the bottom of the plate tower serving as a Gay Lussac tower upon the top of the Glover tower, the former being placed at a convenient height for that purpose. This would have been impossible if the Gay Lussac had been an ordinary fifty or sixty foot coke tower. The matter might have been arranged just as easily in the opposite way.

The most important and interesting application of the plate column in the manufacture of sulphuric acid is that for diminishing chamber space. Every theory of the lead chamber process, worthy of such a name, supposes a constant interaction of the gases and the liquid portions floating in the chamber atmosphere in the shape of mist. Before that action is completed in the ordinary lead chambers, the ingredients must remain a very long time in contact with each other, and must quite gradually cool down, principally owing to the fact that the particles of the mist are separated by comparatively wide spaces and the action of the water or dilute acid on the nitrososulphuric acid is thereby greatly retarded. This drawback had been more or less clearly recognized by many previous inventors, beginning with Gossage, and many endeavors had been made to overcome it. But all these had either completely failed or at least effected their purpose so incompletely that they had been given up again. Thus all proposals for employing coke within the chambers for improving the mixture of the gases have necessarily broken down in consequence of the chemical action of the coke referred to above. Mechanical aspiration of the gases and re-injecting them into the chambers has also failed to improve matters to a great extent. Some little time ago the Thyss process attracted much attention. In this lead towers are interposed between the chambers, filled with lead sieves, but, as might have been foreseen, the lead sieves were soon stopped up by lead sulphate and quickly destroyed. The Delplace chamber is another attempt to produce a better mixture of the gases, but it can not attain this end at all completely or much better than any lead chamber of the old type.

By adapting my plate column to this special end, I believe, I have solved the problem more efficiently than any of my predecessors. I based my proposal on the fact, first securely established by myself, together with Dr. Naef, that the rate of formation of the acid within the first chamber of a set is very unequal. This was proved by very numerous observations and analyses, carried on at a Swiss works for several months, and afterwards confirmed at other places by a number of entirely independent observers. The curve of acid formation rises rapidly to a certain height, but about midways in a 100-foot chamber it flattens and turns nearly to the horizontal, so that the second half of the chamber performs very little work indeed. But as soon as the gases pass over into the second chamber, the formation of sulphuric acid is suddenly revived, thus proving that the contact of the gases and vapors with the end wall of the chamber, and their compression in the connecting pipe exerts a very favorable influence on their interaction. Most probably several conditions are at work here. The shock of the vapors against the solid surfaces, by which the sundry particles forming in their separation a fog or mist are brought together and are made to interact; further, the better mixture of the gases during their passage through the narrow connecting pipe, and lastly the cooling action of the end wall of the chamber, which cooling, according to the modern theories of the vitriol chamber process, is essential for the production of sulphuric acid from its components. Having thus, as I believed (and I think justly) recognised the causes of the favorable influence exerted by dividing the chamber space into several chambers, and of the revival of the reactions distinctly observable between the first and the second chamber, I proceeded to draw the consequence of these views, by immensely multiplying the conditions found to be conducive to the acid forming process. For this purpose I interposed, like Thyss, a kind of tower between the first and second chamber; but in lieu of simple lead sieves, which produce only an incomplete mixture, and which, as noticed before, are doomed to rapid destruction, I filled my tower with the plates I had previously devised for other purposes, consisting of chemically inattackable material, and by their geometrical design solving in

the completest possible manner the problem of thoroughly dividing the gaseous current, and intimately mixing up its ingredients, together with innumerable shocks against solid surfaces. Even then two conditions for a proper chamber process would be absent, *viz.*, the supply of sufficient moisture, and the keeping down of the temperature below the optimum for the process; and these two conditions I supply simultaneously by feeding the towers with more or less dilute acid, whose evaporation yields both the water and the cooling action necessary for compelling the reaction to take the best possible course.

Theoretically there is no reason why such columns should not take the place of the lead chambers in their entirety. Long ago similar plans have been proposed, and quite recently a Mr. Barbier has again taken out a patent for a system, in which sulphuric acid is made without any lead chambers, in towers filled with earthenware cylinders, and fed with acids of different strength. In principle Barbier's plan does not at all differ from others which have been tried ten or twenty years ago, and have failed. Just that failure, I must confess, has discouraged me from proposing the entire abolition of the lead chambers to other people; but if I possessed a chemical factory of my own, I should certainly have tried that plan with my plate towers three years before Barbier took out his patent, which, of course, cannot be applied to that well-known principle, but only to his special kind of towers. For the present, at any rate, I do not venture to go beyond proposing to cut off the chambers at that point where all observations have proved the reactions to decrease rapidly in intensity, say, at a length of fifty feet, and to replace the remaining length of an ordinary chamber by a plate tower, repeating this arrangement with the second, and if needful with the third chamber of a set.

Up to this time no chamber system has been fitted up according to the plan just described, but in all cases the plate towers have been put between the existing chambers of an ordinary set, where they certainly perform a great deal of work, but evidently much less than could be done with a more perfect arrangement. I have therefore the right to consider the results hitherto obtained as a minimum; and looked at in this light, they are extremely

encouraging, as far as I have been able to ascertain them, in which aim I have been much hampered by the unwillingness of many manufacturers to supply information for the benefit of their competitors. Thus for instance, the United Alkali Company, in England, has erected a plate tower, but I have not been able to extract any information as to the works at which that has been done, and for what purpose, let alone telling me anything about the results obtained therewith. In a few cases, fortunately, I have been favored with more information, and this I will now lay concisely before you.

At a Bohemian works, the first where this plan has been adopted, and where, consequently, the best conditions were not yet ascertained, the plate column has raised the quantity of pyrites burnt to an additional thirty per cent. Beyond this it is impossible to go in that place, as there is no more room in the kilns; but as the chamber following the plate column has no work whatever left to do, the acid making process having been completed in the column, the real increase of chamber capacity has been seventy per cent.

At a Dutch acid works there are two sets of chambers of exactly the same dimensions, namely one chamber of 64,400 cubic feet, and another of 19,950 cubic feet following this. In one of the two sets a plate column of ninety-six plates in all has been placed between the two chambers, and this set, I am informed, can be worked as if it held 22,500 cubic feet more than the other, so that each of the ninety-six plates would correspond to a space of 234 cubic feet, that is, more than two hundred times the room occupied by the tower itself.

At Valencia, in Spain, a plate column had been working for eighteen months, when I received the last news about it. That set was then burning forty-two per cent. pyrites in excess of what it had burnt before it had been provided with the column, whilst the consumption of niter had diminished from 2.2 down to 1.7 parts to 100 of fifty-two per cent. pyrites, which signifies a saving of nearly twenty-five per cent. of the niter. The yield of acid is excellent, and could hardly be better in that hot climate, where the first chamber in summer has a temperature

up to 88° C. In the plate column it comes down to 28° or 50° C., and the gases go into the Gay Lussac with 40° C.

Looking at the very imperfect way in which the plate towers have been hitherto adapted to old sets of chambers, it is fair to hope that much better results than even those which I have been able to report would be obtained, if that principle were more thoroughly carried out. Even the present results show an immense superiority over Barbier's system, which, according to his own statement, requires one-sixteenth of the present chamber space, whereas my columns do from 100 to 250 times as much work as the same cube of chamber space. The reason of this great superiority evidently lies in the scientific construction of my plates, compared with the hap-hazard packing of other systems.

Allow me now to say a few words on the employment of plate towers for the condensation of hydrochloric acid. The very first tower which I designed was tried for this purpose, and the experience gained in that trial was utilized for a thorough reconstruction of the system. Since that time several plate towers have been supplied for the same purpose, and a very large one has been delivered just before my leaving Europe; but all information on the subject has been withheld from me, so that I cannot communicate anything on that subject beyond what was observed at the first trial, mentioned above, with the very imperfect kind of columns first used, at the celebrated Griesheim works, one of the most carefully managed alkali works in the world. According to the official report then furnished to me, the following results were obtained. Two superposed columns, of sixty cubic feet each, with a total plate surface of fifty-six feet (reckoning both top and bottom side of the plate) effected the condensation of ninety per cent. of the gases issuing from a salt cake pot, decomposing fourteen hundred weight of salt every four hours. The trial was continued for twenty-four hours in succession; the acid obtained varied from fifteen to twenty-two, and it averaged twenty degrees Baumé at 15° C. In England the smallest condensing space for such a quantity of salt would have been a coke tower of seven by seven by forty feet, holding about 200 cubic feet and possessing a coke surface of about

20,000 superficial feet. Compare that with my sixty cubic or fifty-eight superficial feet which did ninety per cent. of the work!

The coke tower certainly possesses one important advantage over its dwarf rival, the plate tower. The former holds a large stock of liquid, serving as a regulator for the unavoidable inequalities in the composition of the gases, whereas the latter possesses no such regulating stock. But this drawback can and ought to be counteracted by placing in front of the plate tower ten or fifteen stoneware receivers of the usual type, or a few large stone tanks, through which the acid condensed in the plate tower gradually flows onward, and issues from the last of the receivers at full strength; the gases are made to travel the opposite way, *viz.*, first through the receivers, and then through the plate tower. In this case the stock of acid contained in the receivers serves the same purpose as that contained in a coke tower.

Most of the 130 plate columns hitherto sold, serve for another purpose than those I have so far mentioned, *viz.*, for the recovery of nitric acid from the lower oxides of nitrogen by means of contact with air and water. I believe there is a general agreement on the point that no other existing arrangement for that purpose comes up to mine. In 1889, when the Jury of the International Exhibition at Paris listened to an explanation of the new methods for producing chlorine, based on the use of nitric acid, it was taken for granted on all sides that the problem of recovering nitric acid from nitrous fumes had been definitely solved by my apparatus. As far as the manufacture of commercial nitric acid is concerned, it is significant that both the rival inventors of new condensing systems for that acid, Mr. Guttmann and the Griesheim Company, much as they differ in every other way, employ the plate column at the end of their plant, for dealing with the nitrous vapors. In the just-mentioned case only a few per cent. of the total acid pass through the column; but in all those cases where nitric acid is employed as an oxidizing agent, and where the lower nitrogen oxides, evolved in that process, had been formerly lost, or only quite incompletely recovered, the plate column now steps in as the coping stone of the edifice. Instances of this kind are the production of chlorine in any one

of the processes doing this by the aid of nitric acid, with or without the intervention of manganese or other agents; the manufacture of arsenic acid from white arsenic, or of phthalic acid from naphthalene tetrachloride; the manufacture of iron mordant for dyeing purposes; that of blue copperas from metallic copper, and too many other cases to be enumerated here. Formerly, whenever the treatment of nitrous gases was at all attempted, this was done by a string of perhaps a hundred separate receivers, or by a coke tower, the latter being saddled with the great drawback already mentioned, *viz.*, its reducing action, in a case where the very opposite action is called for. In the March number of the *Journal of the Society of Chemical Industry*, Mr. Guttmann mentions the fact that at the works managed by him a small plate tower, ten feet high, performed the work formerly done by a coke tower forty-eight feet high, but much better; for the former made acid of 40°, the coke tower only such of 30°, and the plate tower actually satisfied the requirements of the Government Inspector, concerning the complete condensation of the nitrous gases, better than any other known apparatus.

In conclusion I beg to point out one more interesting use of plate columns. When gases have to be dried, by bringing them into contact with moderately concentrated sulphuric acid, which has generally been done by coke towers, the plate column is most evidently in its proper sphere, on account of its cleanliness, its chemical resistance to any attack, and the inconsiderable height to which the acid has to be pumped.

Many other uses of the plate column will no doubt suggest themselves to the industrial chemist; but I will bring my remarks to a close, and not detain you any longer with my invention.

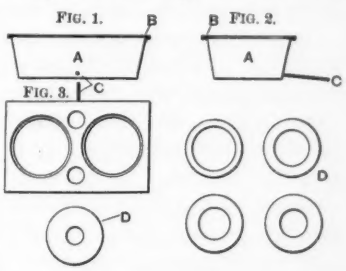
DESIGN FOR WATER BATH.

By A. W. Nibelius.

THE following is a description of a water bath with constant water level, which I have found to be satisfactory in practical work:

Fig. 1 represents a longitudinal and Fig. 2 a transverse sec-

tion, and Fig. 3 a plan view of the bath. A is a common sheet iron "dripping pan" of the hardware trade, 10 x 6¼ inches at the top and three inches deep, transformed by enamelling into so-called agate ware. C is a brass tube ¼ inch outside and ⅛ inch inside diameter, and 3½ inches long, soldered fast near the bottom of the pan and connected by a $\frac{3}{16}$ inch rubber tube with the constant water level apparatus. The tube is inclined somewhat, so as to prevent steam bubbles remaining therein and thus interfering with the siphon action. On the pan is loosely laid a ¼ inch thick china plate, B, in which are two 4 and two 1 inch holes, the latter, when not in use, to be covered with china crucible covers. In the former fit five china rings (D) with holes of the following diameters: 3, $2\frac{5}{8}$, $2\frac{5}{16}$, 2, and $1\frac{9}{16}$ inches, into which will fit respectively No. 3, No. 2, No. 1, No. 0, and No. 00 Griffin's low wide shaped beaker glasses. On the rim of the three inch hole in the china ring a No. 4 and a No. 5 beaker can be placed, and on the rim of the four inch hole in the plate can rest a No. 6 and a No. 7 beaker. Of course, only one ring at a time can rest on the flange of the large holes in the plate.



By means of the constant water level apparatus the water in the pan is kept at a uniform depth of 1½ inch, and in order to keep this quantity of water constantly boiling it will be necessary to employ the flame of a kerosene oil stove having a four inch wick, or one Bunsen burner.

I have found this water bath to be clean, of reasonable price and sufficiently large for one laborant doing ordinary laboratory work.

Messrs. Eimer and Amend, of New York City, will furnish the above described water bath, they having arranged to have the china plate and rings made by the Royal China Works, of Berlin.

LABORATORY, HACKETTSTOWN ZINC CO.,
HACKETTSTOWN, N. J., JULY, 1893.

CERTAIN DISTINCT ADVANCES IN THE ANALYTICAL CHEMISTRY OF RECENT YEARS.[1]

By Albert B. Prescott.

OF the important gains made by the present generation of chemists let us acknowledge (1) the resolute attempt to find out the composition of matter as a whole in any and all of its mixtures of whatever source.

Analytical workers have undertaken to resolve the complex mass and account for all its contents. It has been their ambition to identify and determine existing molecules of every sort within a given mixture, while synthetical workers have sought to reach the constitution of the molecules themselves. The task of complete analysis has been entered upon, that called "proximate" as well as that called "ultimate." There have been good investigations that have taken "extractive matter" and "empyreumatic matter" and "bituminous matter" and other undetermined residues as subjects for the beginning of chemical work rather than the end of it. The task of the complete analysis of matter in its every possible portion is a task that has been recognized and entered upon as a necessity of chemical advancement.

I do not by any means infer that the determination of distinct compounds is the result of analytical chemistry alone, as but one of the divisions of the science. On the contrary I would emphasize the dependence of the analyst upon the entire body of chemical learning. He is limited by this dependence even for the identification and estimation of distinct bodies without going into the make-up of molecules. Analysis is or ought to be a certain function of the whole body of chemistry, not a part of the body which could live if separated. An analyst can not well be less than a whole chemist, and though his ends be single in direction, they are not indifferent to the powers common to all chemical insight.

The analytic method began to yield large returns in the last century. When Black made more exact qualitative examination of fixed air he began to uncover that chain of underlying truth laid hold of by Priestley and fairly dislodged by Lavoisier and other contemporaries. In the first half of this century the

[1] Read before the World's Congress of Chemists, August 22, 1893.

enormous analytical detail instituted by Berzelius extended the very foundations of physical science. And in the present generation the analyses of biological chemists and industrial chemists of many and various purposes have been very influential factors in the support of great principles of chemical truth.

Again, the courage of analytical effort in recent years has been seen especially

(2) In the elaboration of methods for the isolation of carbon compounds, both natural and artificial. "Proximate organic analysis" is not so greatly at a discount as it was twenty years ago. Research has been devoted to the estimation of organic compounds, unbroken and unaltered. It has been a common necessity to effect determinations truly "proximate," in the definition of this inadequate word. There have been pointed inquiries from the biologist often, from the metallurgist at times, from the theoretical chemist not seldom, what is the chemical character of this body as its exists just before its analysis? Since Dragendorff devised ways of plant analysis, and Hoppe-Seyler collected methods of physiological analysis, thousands of contributions have enriched the resources of the organic analyst and thousands of workers are now in like endeavor. Chemical literature is thickly strewn with directions for analysis to the end of the identification of the integral molecule, representing matter in its living state, if such a figure of speech may be used. This is indeed the special task of analytical research, although the terms of analysis are also given to operations that accompany synthetic work, to wit:

(3) In studies of the molecular structure of bodies produced by nature, bodies mineral, vegetable, and animal, as well as those of artificial production. To classify analytical work strictly by definition, which, however, I have no desire to do, all the studies of molecular constitution come within the range of analytical inquiry. But even under customary classification of chemical labor, it will be observed that certain instruments of observation early used by analytical chemists have since been found most effective in studies of molecular structure even for what is termed the configuration of the molecule. Especially, therefore,

(4) In the employment of physical methods of inspection, whereby molecular change is avoided, important advances have been made in the analyses of recent years.

First of all through the several responses of the molecule to light, under more exact observation, the clearest of identifications have been obtained. Optical methods have multiplied and become more exact. We are, however, only in the beginning of their adaptation to analysis. Studies of geometric isomerism have shown the analyst how rich in results the polarimeter may become. Next to this, probably, stands the refractometer in its value as a means of recognition in analysis. Then the use of the spectroscope for studies of absorption by transparent bodies has already done admirable service to analysis, both organic and inorganic. New responses of matter to heat have been brought under observation. In qualitative determination, as in the finding of the molecular mass, the freezing point and the effect on solidifying points of solvents are in question as well as the melting points and boiling points. The chemical world is alive with interest in the advances of the new physical chemistry. To these advances no one is and is to be more indebted than the analyst. Solubility itself, the great common factor of analytical operation, is under investigations in which the analyst has the keenest interest. The feebler influences of adhesion, too often overlooked, causing waste in quantitative separations and putting limits upon the best of our results for analytical recovery, these, with the phenomena of capillarity, are well under investigation. The very checks of control analyses serve as data for studies in molecular physics.

It is not possible for me to group together in classes near all the ways of advance in recent analytical chemistry, and I will but specify once more how this advance appears

(5) In the reciprocal benefits of scientific research and of technical skill. We see this in the work of experts, those in biological and pathological analysis, sanitary and forensic analysis, industrial and commercial analysis, agricultural and metallurgical analysis. Chemical literature during the last ten years shows how promptly discoveries like those of Emil Fischer in the sugar group, or those of Ladenburg upon hydrolysis of

alkaloids, those of Gladstone on refraction equivalents, or those of Baeyer upon the phthaleins, become well reduced to practice in the operations of analytical work. The simple volumetric estimations of acid and alkali are expanded in ten-fold application in thousands of analytical laboratories by means of varied indicators from the color discoveries of coal tar chemists such as Otto Witt. Analysis bows its acknowledgment of indebtedness to synthetic research. The interests of the section of analytical chemistry are all interwoven with the interests of all the sections of this congress. The analytical chemist will be a good listener to all the papers in the rich and varied repertory of the week before us.

ON THE ARTIFICIAL PRODUCTION OF PETROLEUM.

By Dr. C. Engler.

SCIENTISTS have discussed very often in the last few years the question in which way petroleum, this source of wealth, with its special scientific interest for this country, was formed by nature. According to one theory it is generated from inorganic materials. Sokoloff thinks, that petroleum was produced during the period of the formation of our planet out of cosmical hydrocarbons, which in the beginning dissolved in the soft mass, separated from it later on. Mendelejeff assumes that water entering by fissures and chasms the interior of the earth came in contact with melting carbide of iron and produced so in a simple manner oxide of iron and the hydrocarbons of petroleum. Strong objection cannot be made to these two theories from the chemical standpoint; but the composition of the different kinds of petroleum is against them, and geology considers them not free from objections.

For a series of years the idea that petroleum was produced from the remains of plants by a kind of a distillation process, was most generally adopted, especially by chemists. Chemical and geological reasons are against this theory. From the chemical standpoint it seems quite impossible that the substance of the plants could be split up by distillation into petroleum without

[1] Read before the World's Congress of Chemists, August 23, 1893.

leaving charcoal or coke. There would also be a genetic connection between coal and petroleum; but in occurrences of the ordinary kind, coal is nearly always absent. If this were really the case, then there ought to be with every oil occurrence in close connection a coal bank, which really seldom happens.

By a third theory the remains of animals form the raw materials from which petroleum is formed in nature. There are many facts proving the decay of masses of animals which we find now in banks in the crust of the earth in the form of the remains of shells, fishes, saurians, etc. Prominent scientists, amongst them the Americans, Wrigley, Whitney, Hunt, and others, and in Europe Höfer and Ochsenius especially, defend this idea on geological grounds. But I will not enter into the geological discussion preferring to try to give an answer to the question: How can the transmutation of animal remains into oil be imagined?

In order to answer this some thousands of salt water fishes and also shells have been distilled under strong pressure. The result was a liquid, containing mostly nitrogenous bases, such as pyridin, which was little or not at all similar to petroleum. I then recalled some experiments of Wetherill and Gregory, who found that the wax found in cadavers, the so-called "Adipocere," was nothing else but the fatty residue, which remains after the putrefaction of all the other animal matter, especially of the nitrogenous constituents of the cadaver. It is also well known that even fossil bones frequently contain fat. The question now raised was this: Could not the process in nature have been a similar one; should not first of all the nitrogenated animal substance have been destroyed leaving the fat, which was then transformed into oil. In order to prove chemically this possibility, I submitted animal fat (train-oil) to distillation—first in a sealed glass tube, later on in a large iron vessel—under a pressure of twenty-five atmospheres at a moderate heat (300–400° C.) and to my great delight found that under favorable conditions seventy per cent. of the train oil was transformed into petroleum. This equals ninety per cent. of the theoretical output. Besides the oil some water and some combustible gas was

always formed. The same behavior has been shown by other fats like butter, the fat of hogs, artificial fats, also the chemically pure glycerids of the fats like tri-olein, tri-stearin and the free fatty acids. All could be transformed into petroleum by distillation under pressure, when managed in the proper way.

This liquid, which you see here, is the distillate of the fish oil, and I have isolated from it almost all the hydrocarbons which have been discovered in the petroleum of Pennsylvania. The other products—the oil burning in this small lamp, too—are oils obtained from the crude material by purification.

But not only illuminating oils are produced. I separated also by distillation those lighter hydrocarbons which compose the gasoline, the ligroin, the benzine, etc. Recently I have succeeded in finding and separating paraffin wax and lubricating oils from those parts of the crude oil which show a high boiling point. This removes the objection of O. Ross to my theory of the formation of petroleum from animal remains. As a matter of fact I have found in the distillate obtained by decomposition of train oil, nearly all the constituents which have been separated from the natural crude petroleum, and even the gases, which, like natural gas, consist essentially of marsh gas.

Very recently I have made close investigations on the mechanism or on the chemism of the formation of the hydrocarbons of the petroleum produced by distillation of fat under pressure. This paper is published in a recent number of the *Berichte der deutschen chemischen Gesellschaft*, *1893*, **26,** 1436. These experiments prove that the simpler organic acids split up in the same way, yielding almost the theoretical quantity of the respective hydrocarbon. Thus phenylacetic acid yields toluene. For further details I am obliged to refer to the paper itself. I need only remark, that we have to assume that the acids with high molecular weights are decomposed with the production of a number of hydrocarbons.

To recapitulate, it is a geological fact that we find in nature the remains of antidiluvian animals as shells, fishes, saurians accumulated in masses. Whether these animals have been piled up in consequence of a natural super-production in special places in the ocean, or by currents, or in consequence of great

revolutions of the earth, this must be decided by geology; but the remains exist.

Now in which manner do the organic substances of these animals become decomposed?

The animal substance consists essentially of nitrogenated material and fat. The former is easily decomposed, the latter is very stable, a fact which has been very well known for a long time and has been shown again by exact investigations. Therefore we find the wax of cadavers in old graves, therefore the fat in the bones of mammals thousands of years old, therefore the fat on the bottom of the ocean recently found.

Whether and how far the fat was decomposed in this long period by the water splitting up glycerol and forming the free acid, for instance the fat in the bones of mammals, cannot be answered. Both, fat as well as the fatty acids form petroleum, when distilled under pressure.

We can imagine, that such remains wrapped in mud and transported by the currents in the ocean, easily accumulate and later on, under the pressure of sedimentary layers or strata, perhaps under the influence of heat too, are transformed into petroleum. This is only one of the many possibilities by which the mechanical process of the transmutation of fat into petroleum may have happened.

Under any circumstances I think I have proven that from the chemical standpoint, the formation of petroleum from animal remains has the greatest probability, as we are able now to transform every animal fat into petroleum.

THE DETERMINATION OF PHOSPHORIC ACID BY THE TITRATION OF THE YELLOW PRECIPITATE WITH STANDARD ALKALI.[1]

By Henry Pemberton, Jr.

IN the year 1882, I described a process for determining phosphoric acid, volumetrically, by ammonium molybdate, on the principle of Wildenstein's sulphuric acid determination, or of Gay Lussac's silver method. An *aqueous* solution of am-

[1] Read at the stated meeting of the Chemical Section of the Franklin Institute, held September 19, 1893. Communicated by the author.

monium molybdate is run into the solution of the phosphate until no futher precipitate is formed.

But it is not of this process that I now have to speak. It is referred to here, in order to draw attention to the concluding paragraph of the paper, as follows:

"I have obtained very sharp and accurate results by determining the amount of yellow precipitate (formed as above, after thorough washing), by means of a standard solution of caustic alkali, using litmus as an indicator; a description of which I hope to present in a future paper. I mention it here simply to place the fact on record." (*Journ. Frank. Inst.*, **113,** 193; *Chem. News*, **46,** 7.)

At that time I did a considerable amount of work upon the last-mentioned process, with very satisfactory results. A study was made of the conditions most favorable to obtaining a phosphomolybdate precipitate of constant composition, using solutions of disodium hydrogen phosphate of known strength, and also a solution of apatite, the determinations being checked by standard methods.

Before the process was in shape for publication, however, my attention was called to work of an entirely different nature, and no description of the method was published other than that embodied in the above-quoted paragraph.

Since that time several chemists have described processes based upon the same principle.

E. Thilo, in the analysis of Thomas slag (*Chem. Ztg.*, **11,** 193), dissolves the yellow precipitate in standard ammonia, and titrates back with acid, using litmus as an indicator.

Franz Hundeshagen (*Ztschr. anal. Chem.*, **28,** 171) uses standard sodium hydroxide in excess, and titrates back with nitric acid, using phenolphthalein as an indicator.

C. E. Manby (*J. Anal. Appl. Chem.*, **6,** 82) determines the phosphorus in steel, iron, and iron ores, by dissolving the yellow precipitate in ammonia, acidifying with nitric acid, evaporating to dryness, and heating gently to expel nitric acid and ammonim nitrate. He then titrates, using the same solution and indicator as Hundeshagen employs.

James O. Handy (*J. Anal. Appl. Chem.*, **6,** 204) avoids

the evaporation and heating and titrates directly as Thilo and Hundeshagen do, using standard soda and phenolphthalein. M. Rothberg and W. A. Auchinvole (*J. Anal. Appl. Chem.*, **6**, 243) also describe the same process.

Although it is now eleven years since I drew attention to this process, its advantages are so great that any information touching it, in addition to that furnished by the foregoing chemists, may be of interest. It far surpasses in quickness the process described by me (on the Gay Lussac or Wildenstein principle) and at the same time lacks nothing in accuracy. In most of the papers of the above-mentioned chemists, the process is applied to the determination of phosphorus in small quantities, as it occurs, for instance, in iron, steel, or ores. During the past year, I have had occasion to apply it to the examination of a number of phosphate rocks, as well as of strong solutions of phosphoric acid, containing over fifty per cent. P_2O_5 and the method has been used continuously during that time. I am indebted to Mr. Edwin Harris, who had charge of most of the laboratory work of the factory, for many of the figures given below. It was seldom that two tests of the same material differed more than 0.1 per cent. in P_2O_5 even when the total P_2O_5 present amounted to as much as forty per cent. to fifty per cent. of the substance analyzed.

The following solutions are used:

Ammonium Molybdate.—Ninety grams of the crystals are dissolved (in a large beaker) in somewhat less than one liter of water. This is allowed to settle, over night, and the clear liquor decanted into a liter flask. The small quantity of insoluble molybdic acid, always present, is dissolved in a little ammonia and added to the main solution. Should the molybdate be found to contain traces of P_2O_5, a few decigrams of magnesium sulphate are added, ammonia being added to faint alkalinity. The whole is then made up to one liter. It is this *aqueous* solution that is used, *no nitric acid whatever being employed.* Each cc. precipitates three milligrams of P_2O_5.

The *ammonium nitrate* solution is simply a saturated aqueous solution of the salt. Distilled water is poured into the bottle of crystals in quantity insufficient to dissolve them all. Even in

cold weather, ten cc. of this solution is amply sufficient for each test.

The *nitric acid*, used for acidifying the solution of the phosphate, has a specific gravity of 1.4 or thereabouts.

The *standard potassium hydroxide* solution is of such strength that one cc. = one mgm. P_2O_5. One hundred cc. of it will neutralize 32.65 cc. of normal acid. It can be made from normal potassium hydroxide (that has been freed from all carbonate by barium hydroxide), by diluting 326.5 cc. to one liter. But its strength is best determined empirically by a direct test upon a phosphate solution of known strength, precipitating with ammonium molybdate and making the analysis as described below, all potassium carbonate having first been removed by barium hydroxide.

The *standard acid* has the same strength, volume for volume, as the potassium hydroxide and can be made by diluting 326.5 cc. of normal acid to one liter. In testing it against the alkali, phenolphthalein (and methyl orange) should be used.

The *indicator* can be either litmus, rosolic acid, or phenolphthalein. I have used the latter almost exclusively, as it has been shown, by J. H. Long (*Am. Chem. J.*, **11**, 84) that titrations with this indicator in the presence of ammonium salts are perfectly reliable if the amount of the ammonium salt present is not excessive, if the solution is cold, and if the phenolphthalein is used in sufficient quantity. One gram of the phenolphthalein is, accordingly, dissolved in 100 cc. of sixty per cent. alcohol, and at least 0.5 cc. of this solution is used for each titration. The washing of the ammonium phospho-molybdate is done by water. (Isbert and Stutzer, *Ztschr. anal. Chem.*, **26**, 584.) It may be of interest to quote from their results, since it is by some chemists thought necessary to wash with a neutral or acid solution of an ammonium salt. In all tests, as made by them, twenty-five cc. of the sodium phosphate solution were precipitated by ammonium molybdate and the phosphoric acid determined therefrom, as magnesium pyrophosphate in the usual manner.

When the yellow precipitate was washed with ammonium nitrate solution, there were obtained:

(1)..... 0.1943 gram P_2O_5 in 50 cc.
(2)..... 0.1948 gram P_2O_5 in 50 cc.

When washed with water, there was found:

(3)..... 0.1947 gram P_2O_5 in 50 cc.
(4)..... 0.1942 gram P_2O_5 in 50 cc.

In order to establish the fact more certainly, the precipitate was washed with unusually large quantities of water:

	cc. of water used in washing.	P_2O_5 found.
(5).....	300	0.1947 in 50 cc.
(6).....	400	0.1944 in 50 cc.
(7).....	500	0.1948 in 50 cc.
(8).....	1,000	0.1940 in 50 cc.

There is, accordingly, no danger of loss in washing the yellow precipitate with water.

The following is the method of performing the analysis:

One gram of the phosphate is dissolved in nitric acid, an excess of which can be used with impunity, and the solution filtered into a 250 cc. flask and made up to the mark. The solution can even be poured into the flask without filtering, since the presence of a little insoluble matter does not interfere in the least with the titration. Moreover, since most phosphate rocks seldom contain over ten per cent. of insoluble matter, and as this has the sp. gr. of at least 2, it occupies a volume of about 0.05 cc., an amount so small that it may be neglected. (For instance, even in the case of a phosphate rock containing forty per cent. P_2O_5, the error is only 0.008 per cent. P_2O_5.)

After the clear solution has been poured off, it is well to treat the sand, etc., at the bottom of the beaker, with a cc. or so of hydrochloric acid, in the warmth, to insure complete solution.

It is not necessary to evaporate to dryness. Isbert and Stutzer have shown, in their paper, that when the yellow precipitate is washed with water, the soluble silica is removed, and that evaporation (to render the silica insoluble) is superfluous. Their results are corroborated by the test analysis that will be given below. In the event of its being desirable to remove silica by evaporation, for any purpose, the evaporation should be performed over a water bath, or, if on an iron plate, with great care, since, otherwise, meta or pyro phosphates are formed with results that are correspondingly low.

Twenty-five cc. of the solution (equal to 0.1 gram) are now

taken for analysis. It may be thought, by some, that an analysis made upon so small a quantity of material as one decigram, and with a standard solution representing only one milligram per cc., may be liable to errors that would not exist, when using larger quantities or stronger solutions. But it should be borne in mind that the accuracy of measurement with a twenty-five cc. pipette, is precisely the same, whether ten grams of the original substance are taken or only one gram. Any error in measuring with a pipette is, of course, entirely independent of the quantity in solution. In regard to the amount of material to be manipulated (filtered, washed, etc.) it will be remembered that the weight of the yellow precipitate is over twenty-eight times the weight of the P_2O_5 contained in it. Every milligram of P_2O_5 is accordingly represented by more than twenty-eight milligrams of precipitate. The standard alkali, although representing only 0.001 gram per cc. is in reality more than three times as strong as the decinormal solution generally employed. Of course, in the case of materials containing only ten to fifteen per cent. P_2O_5, as in fertilizers, two or three grams can be taken for analysis, if desired, instead of one gram.

Returning, therefore, to the method of the analysis, twenty-five cc. of the solution are measured out and delivered into a beaker holding not more than 100 to 125 cc. A large beaker requires unnecessary washing to remove the free acid in washing the yellow precipitate. The solution is neutralized with ammonia—until a precipitate just begins to form—and five cc. of nitric acid of sp. gr. 1.4 added. Ten cc. of the ammonium nitrate solution are added, and the entire bulk of the solution made up to fifty to seventy-five cc. by adding water.

Heat is now applied and the solution brought to a full boil. It is then removed from the lamp, no more heat being applied and treated *at once*, with five cc. of the aqueous solution of ammonium molybdate, which is run into it from a five cc. volume pipette, the solution being stirred as the precipitate is added. The beaker is now allowed to rest quietly for about one minute, during which time the precipitate settles almost completely. The five cc. pipette is filled with the molybdate solution, and a part of its contents allowed to drop in, holding the beaker up

to the light. If a formation of a yellow cloud takes place, it is at once perceptible, in which case the remainder of the pipette full is run in, the solution stirred and allowed to settle. A third pipette full is now added as before. Should it cause no further cloud, only about one-half of its contents is added, the remainder being run into the beaker into which the filtrate and washings from the yellow precipitate are to go. In the test analyses given below, it will be shown that even when *fifteen cc. in excess* of the molybdate, were purposely used, over and above the calculated amount, the results were accurate—no molybdic acid coming down with the yellow precipitate.

It is seldom that more than fifteen cc. in all (three five cc. pipettes full) of the molybdate have to be added. Since each cc. precipitates three milligrams P_2O_5, fifteen cc. will precipitate forty-five milligrams P_2O_5. This is equivalent to forty-five per cent. on the 0.1 gram taken for analysis, and it is not often that any material to be examined contains over this percentage. In the analysis of materials rich in phosphoric acid, it is one of the embarrassing features of the usual process, in which the *nitric acid solution* of the molybdate is used, that, in the first place, large quantities of the precipitant have to be used (frequently several hundred cc.), and, in the second place, that the analyst is never certain that enough has been added to throw down all of the phosphoric acid. This necessitates frequent testings of small portions of the phosphate solution, or of the filtrate. There is another difficulty peculiar to the process as usually carried out in all methods in which the determination is made directly upon the phospho-molybdate itself, in that much care must be observed to keep the solution at a certain temperature, since otherwise molybdic acid contaminates the precipitate and the analysis is rendered worthless. In the process herein described, using an *aqueous* solution of the molybdate, the point at which sufficient of the precipitant has been added is easily seen. No molybdic acid separates, because, in the first place, no great excess of molybdate is added; and because, in the second place, the solution is filtered immediately, or as soon as it has settled, which requires only a minute or two. The time required from the first addition of the molybdate to the beginning of the filtra-

tion is never over ten minutes, and is generally less. The filtrate and washings from the precipitate when treated with additional molybdate solution, give, on standing on a hot plate for an hour or so, a snow-white precipitate of molybdic acid, showing that all of the phosphoric acid has been precipitated. I have observed this hundreds of times.

A slight correction should be made to the statement made above in regard to fifteen cc. of the molybdate precipitating forty-five milligrams of P_2O_5. This is not strictly true, for the reason that a small quantity (something over one cc.) of the molybdate is required to neutralize the solvent action of the nitric acid. Therefore, in *very* high grade phosphates a fourth five cc. pipette full may be required.

The yellow precipitate is now filtered through a filter seven centimeters in diameter, decanting the clear solution only. This is repeated three or four times, washing down the sides of the beaker, stirring up the precipitate, and washing the filter and sides of the funnel above the filter each time. The precipitate is then transferred to the filter and washed there. When the precipitate is large it cannot be churned up by the wash water and cannot be washed down to the apex of the filter. This is generally the case when there is over ten or fifteen per cent. phosphoric acid present in the substance analyzed. In such an event, I am accustomed to wash the precipitate back into the beaker, and to fill the funnel with water above the level of the filter, doing this two or three times, then washing the precipitate back into the filter. It is not necessary to transfer to the filter the precipitate adhering to the sides of the beaker.

It goes without saying that during the washing no ammonia must be present in the atmosphere of the laboratory. Inasmuch as the beaker, funnel, filter, and precipitate are small, the washing does not take long to perform. It requires, in fact, from ten to fifteen minutes, even when large precipitates (= thirty to forty per cent. P_2O_5) are handled. The precipitate and filter are now transferred together to the beaker. By pressure with the tip of the finger upon the double fold of the filter, it is easily given a sideways motion and lifted out of the funnel without any danger of breakage, the precipitate being still within it.

The alkali solution is run in until the precipitate has dissolved, at least twelve drops of the phenolphthalein (1 : 100) are then added, and the acid run in without delay until the pearly color disappears and the solution is colorless. The presence of the filter paper does not interfere in the least. The reaction of the indicator is not so sharp as when only acid and alkali are used, but it is easy to tell with certainty the difference caused by one drop of either acid or alkali. After deducting the volume of acid used from that of the alkali, the remainder gives the percentage of P_2O_5 directly, each cc. being equal to one per cent. P_2O_5. Thus, if there are 28.3 cc. of alkali consumed, the material contains 28.3 per cent. P_2O_5 when one decigram is taken for analysis. From the time the twenty-five cc. are measured out until the result is obtained, from thirty to forty minutes are required.

I have applied this process to determinations of phosphoric acid in phosphates and fertilizers, and have had no experience in determining phosphorus in iron, steel, or iron ores. I am inclined to believe that in the presence of such large quantities of iron salts when using the *aqueous* solution of the molybdate it may be necessary to guard against contamination of the yellow precipitate by ferric hydrate, perhaps by using larger quantities of nitric acid than five cc., and perhaps by washing the precipitate at first, with dilute nitric acid. It may also be the case that the yellow precipitate will form more slowly.

The following analytical experiments were made in order to test the process.

Several sodium phosphate solutions were used at first, the strength of which was only approximately known, as the aim was to see how closely two readings would agree; equal quantities of the phosphate being taken for each pair of tests.

A.

	cc.
(1) KHO with rosolic acid	15.0
(2) KHO with rosolic acid	15.15

B.

	cc.
(1) KHO rosolic acid	30.5
(2) KHO rosolic acid	30.5
(3) KHO phenolphthalein	30.7

All titrations, after this, were made with phenolphthalein.

C.

	cc.
(1) KHO	31.7
(2) KHO	31.8

A KHO solution was now made of such strength that one cc. = one mgm. P_2O_5.

D.

	mgm.
(1) P_2O_5	50.35
(2) P_2O_5	50.55
(3) P_2O_5	50.40

E.

	mgm.
(1) P_2O_5	51.6
(2) P_2O_5	51.55

F.

	mgm.
(1) P_2O_5	51.05
(2) P_2O_5	50.93

D, E, and F were solutions used in standardizing.

Two different samples of Florida phosphate rock were examined.

I.

	Per cent.
(1) P_2O_5	= 29.68
(2) P_2O_5	= 29.84

II.

(1) P_2O_5	= 31.28
(2) P_2O_5	= 31.34

The following were solutions of phosphoric acid:

I.

	Per cent.
(1) P_2O_5	= 46.78
(2) P_2O_5	= 46.69

II.

(1) P_2O_5	= 44.41
(2) P_2O_5	= 44.63

III.

(1) P_2O_5	= 48.95
(2) P_2O_5	= 48.80

The effect of an excess of ammonium molybdate was tried. The soluble part of an acid phosphate was made up to a definite volume and fifty cc. taken for analysis. It was found to contain 8.28 per cent. P_2O_5. The test was repeated, using fifteen

cc. of the molybdate more than was used in the first trial. Result = 8.36 per cent. P_2O_5 equal to a difference of 0.08 per cent.

The following tests show that it is not necessary to remove silicic acid by evaporating to dryness before precipitating with the ammonium molybdate.

A sample of Florida phoshate rock contained:

	Per cent.
(1) P_2O_5 silica removed	31.21
(2) P_2O_5 silica not removed	31.21

Another sample of the same rock was also tried:

Silica removed.	Per cent.
(1) P_2O_5	= 30.5
(2) P_2O_5	= 30.7
Average P_2O_5	= 30.6

Silica not removed.	Per cent.
(1) P_2O_5	30.6
(2) P_2O_5	30.7
Average P_2O_5	30.65

When silica is not removed the filtrate from the yellow precipitate has a yellow tinge.

The relation between the P_2O_5 in the precipitate and the potassium hydrate was established by determining the strength of a solution of disodium hydrogen phosphate by precipitation as the ammonium magnesium salt, and also by testing it by this titration process. The phosphate of soda solution was weighed (not measured), and the magnesia precipitate, after filtering, was dissolved and reprecipitated with ammonia. (Gooch, *Am. Chem. J.*, **1**, 405.) The results are given in Table I, the last column giving the amounts of P_2O_5 obtained on a basis of ten grams of the solution:

TABLE I.

	Weight of Na_2HPO_4 solution. Grams.	Weight of $Mg_2P_2O_7$ obtained. Grams.	Equal to P_2O_5. Grams.	Grams P_2O_5 in 10 grams of solution.
I.....	75.824	1.2471	0.7956	0.10494
II.....	101.167	1.6637	1.0614	0.10492
III.....	101.622	1.6733	1.0676	0.10505
Average				0.10497

Therefore, ten grams of the solution contain 0.10497 gram P_2O_5.

Weighed portions of the same solution were now precipitated with molybdate and the precipitate titrated with alkali. The results are given in Table II, the last column of which gives the number of cc. of alkali equivalent to ten grams of the solution. The indicator was phenolphthalein:

TABLE II.

	Weight of Na_2HPO_4 solution. Grams.	Number of cc. of KHO sol. required.	= Number of cc. KHO sol. required for 10 grams solution.
I	7.4975	79.05	= 105.4
II	7.8255	82.40	= 105.3
Average			= 105.35

It follows, therefore, that 105.35 cc. alkali = 0.10497 gram P_2O_5; therefore,

(1) 100 cc. alkali = 99.64 milligrams P_2O_5.

The HCl solution was now titrated against the alkali, using phenolphthalein as the indicator. 99.00 cc. alkali were found to equal 99.05 cc. acid.

The HCl was then standardized against pure sodium carbonate.

(With methyl orange, cold:)

(*a*) 1.1291 grams Na_2CO_3 = 65.45 cc. HCl

(With phenolphthalein, boiling:)

(*b*) 1.1934 grams Na_2CO_3 = 69.2 cc. HCl

Therefore, 100 cc. =

(*a*) 1725. milligrams Na_2CO_3

(*b*) 1725. milligrams Na_2CO_3

Since 99.00 alkali = 99.05 acid, it follows that:

(2) 100 cc. alkali = 1726 milligrams Na_2CO_3

It has already been shown by (1) that 100 cc. alkali = 99.64 milligrams P_2O_5. Therefore, combining (1) and (2) we obtain 99.64 milligrams P_2O_5 = 1726. milligrams Na_2CO_3.

Dividing each by its molecular weight, we have:

for P_2O_5 ..... $\frac{99.64}{142.06} = 0.7014$

for Na_2CO_3 ..... $\frac{1726}{106.1} = 16.27$

Therefore $P_2O_5 : Na_2CO_3 = 0.7014 : 16.27 = 1 : 23.2$.

In other words, 23.2 molecules of Na_2CO_3 are required to neutralize the yellow precipitate containing one molecule P_2O_5.

The above figures are based upon the following atomic weights:

Mg ..... = 24.3
O ..... = 16
P ..... = 31.03
Na ..... = 23.05
C ..... = 12

$Mg_2P_2O_7 = 63.80$ per cent. P_2O_5.

There is some uncertainty as to the correct atomic weight of magnesium. If Mg = 24 (instead of 24.3 as taken above) with $Mg_2P_2O_7 = 63.98$ per cent. P_2O_5 the ratio of Na_2CO_3 to P_2O_5 = 23.1 to 1 (instead of 23.2 to 1). It is difficult to obtain absolutely pure Na_2CO_3; any impurity in it will make the ratio of Na_2CO_3 to P_2O_5 too high.

Practically, therefore, twenty-three molecules of Na_2CO_3 are required for one molecule P_2O_5. This agrees with Hundeshagen's results.

I have never seen any explanation as to why twenty-three molecules of alkali are required to neutralize one molecule of the ammonium phospho-molybdate. A discussion of the subject, therefore, may be of interest. Hundeshagen has shown (*loc. cit.*) that (neglecting any water of crystallization) the yellow precipitate, after thorough washing with water, has the following composition:

$$PO_4$$
$$12\ MoO_3$$
$$3\ NH_4$$

Or, doubling the formula, for the sake of clearness:

$$P_2O_8$$
$$24\ MoO_3$$
$$6\ NH_4$$

R. T. Thomson has shown in his researches on indicators (*Chem. News*, **47**, 127) that of the three hydrogen atoms in H_3PO_4 two must be saturated with alkali before the reaction with phenolphthalein will be neutral, the next drop of alkali after this causing the red color to appear. Writing the formula

differently, $H_6P_2O_8$ must become $R_4H_2P_2O_8$ (R being the radical NH_4, or any alkali metal). Therefore, when the yellow precipitate is broken up by alkali, only four of the six molecules of NH_4 are required to form (with the P_2O_5 of the precipitate) a phosphate of ammonium that is neutral to the indicator. The remaining two molecules of NH_4 unite with one molecule of MoO_3, yielding also a salt that is of neutral reaction. This leaves twenty-three molecules of MoO_3, representing the "net available acidity" (if I may use the expression) of the ammonium phosphomolybdate. These twenty-three molecules of MoO_3, of course, require twenty-three molecules of Na_2CO_3 (or its equivalent of KHO) to form Na_2MoO_4. Q. E. D. The following is the formula representing the reaction:

$$6NH_4.P_2O_5.24MoO_3 + 23Na_2CO_3 + H_2O =$$
$$(NH_4)_4.H_2P_2O_8 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23CO_2$$

It may be well to give a short résumé of this method. One gram of phosphate rock, or two or three grams of fertilizer are dissolved in nitric acid, and without evaporating to dryness diluted to 250 cc. The solution need not be filtered. Twenty-five cc. of the solution are delivered into a four-ounce beaker and neutralized with ammonia—until a precipitate just begins to form—and then treated with five cc. of HNO_3 of 1.4 specific gravity. Ten cc. of a saturated solution of ammonium nitrate are added and the solution diluted to a volume of fifty to seventy-five cc. It is then brought to a full boil, removed from the lamp and five cc. of the *aqueous* solution of ammonium molybdate added. This is followed by a second and a third five cc., if necessary, the precipitate allowed to settle, and filtered at once through a seven centimeter diameter filter. It is washed thoroughly with water by decantation and on the filter. The filter and precipitate are transferred bodily to the beaker. Standard alkali is then run in and at least 0.5 cc. of phenolphthalein (one per cent. solution) added, and then standard acid, until the color vanishes. Each cc. of alkali equals one milligram of phosphorus pentoxide.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

A MODIFICATION of the stannous chloride method for iron titrations has been proposed by R. W. Mahon (*Am. Chem. J.*, **15**, 360): If mercuric and platinic chlorides are added to a solution of ferric chloride, strongly acid with hydrochloric acid, at or near the boiling point, stannous chloride reduces all the iron first, and the first drops in excess cause the formation of a faint cloud of mercurous chloride, darkened and rendered instantly perceptible by finely divided mercury and platinum which are precipitated at the same time. A very minute trace of platinic chloride present in solution is sufficient to bring about this reaction. This mixture, then, of mercuric and platinic chlorides, is an indicator which can be used to advantage in titrations of iron by stannous chloride. The indicator can be made from solutions of platinic chloride and mercuric chloride to contain in one liter, 0.05 gram metallic platinum and 34.0 grams mercuric chloride. Fifteen cc. is a suitable quantity to be used in each estimation.

The standard solution of ferric chloride is advantageously made of such strength that one cc. contains 0.01 gram iron, the stannous chloride solution of approximately the same strength. The determination of iron in its ores is made as follows: Weigh accurately about one gram of ore into a 250 cc. beaker. Cover with a watch glass and digest in twenty cc. hydrochloric acid of 1.20 sp. gr. until decomposed. Add now 0.3 gram of potassium chlorate and digest a few minutes longer. The glass and rim of the beaker are washed down into the solution, which should now be about forty cc. in volume. It is filtered and washed into an Erlenmeyer flask; twenty to thirty cc. hydrochloric acid of 1.20 sp. gr. are added to the solution bringing its volume up to about 125 cc. Now add fifteen cc. of the indicator solution and it is ready for titration. Heat the covered solution to boiling. The trace of chlorine remaining escapes. Lower the light and titrate at incipient boiling. The burette should be of 100 cc. capacity.

The residue is prepared for titration by fusing with sodium carbonate, extracting with water and acid, and adding fifteen cc. indicator.

THE ATOMIC WEIGHT OF MOLYBDENUM.

By Edgar F. Smith and Philip Maas.

Received September 25, 1893.

THE present atomic value assigned this element is based upon the results obtained by Dumas (*Ann. Chem.*, **105,** 84, and **113,** 23), Debray (*Compt. rend.*, **66,** 734) and Lothar Meyer (*Ann. Chem.*, **169,** 365). The method pursued by Dumas consisted in the reduction of molybdenum trioxide. Debray also adopted this procedure, but in addition made several experiments upon the precipitation of the trioxide in an ammoniacal solution by silver nitrate. Lothar Meyer's value (95.9) is deduced from results obtained by Liechti and Kemp (*Ann. Chem.*, **169,** 344) in their analyses of the chlorides $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke (A Recalculation of the Atomic Weights, Washington, 1882) expresses the opinion that the most reliable results are those obtained by the reduction of the trioxide. Of the works of Liechti and Kemp he remarks, "traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weights." Rammelsberg (*Ber. d. chem. Ges.*, **10,** 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be 96.18.

Thinking that additional light could be thrown upon the magnitude of this constant, by proceeding in a different direction, we utilized a reaction first observed by Debray (*Compt. rend.*, **46,** 1098, *Ann. Chem.*, **108,** 250), which in the hands of others (Pechard, *Compt. rend.*, **114,** 173; *Ztschr. anorgan. Chem.*, **1,** 262; Smith and Oberholtzer, *J. Am. Chem. Soc.*, **15,** 18, and *Ztschr. anorgan. Chem.*, **4,** 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilized with ease in the form of an hydroxychloride—$MoO_3,2HCl$. Numerous trials have demonstrated that the reaction expressed by the equation, $Na_2MoO_4 + 4HCl = 2NaCl + MoO_3,2HCl + H_2O$, is

quantitative. We exposed pure anhydrous sodium molybdate (at 150–200°) to the action of hydrochloric acid gas, volatilized the molybdenum trioxide, and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We recrystallized it many times, and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates, or alkaline carbonates,—substances that might have been present. The purified salt was dried with extreme care, until no further loss in weight was observed. In this anhydrous condition, it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6.9780. The balance employed by us was of the Sartorius design.[1]

The weights of brass and platinum were of Westphal make and had been previously carefully adjusted for the purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved, was first conducted through a U tube half-filled with damp silver chloride, it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride, and finally through clean cotton, after which it was admitted to the combustion tube, where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150 to 200°C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilized $MoO_3 2HCl$ was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapor repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made, after the

[1] We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, University of Pennsylvania, for the privilege of using this excellent instrument.

boats had remained over night in the dry desiccators, and showed no appreciable alteration. Barometric pressure and temperature were carefully observed and all weighings reduced to the vacuum standard. Our results are as follows:

Na_2MoO_4 in grams.	NaCl. in grams.	Atomic weight of Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078
	Mean	96.087
	Maximum	96.130
	Minimum	96.031
	Difference	0.099

In our calculations we used the following values: $Na = 23.05$, $Cl = 35.45$, and $O = 16$. These have been taken from a revised table of atomic weights published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96.10, the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily, and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than augment the atomic weight found. Another cause of like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result 96.08 obtained by us, approaches very closely to the true atomic magnitude of molybdenum.

UNIVERSITY OF PENNSYLVANIA.
September 16, 1893.

IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

By G. de Laire and Ferd. Tiemann.

(*Continued from page 355.*)

Monacetylirigenin, $C_{18}H_{15}O_8(COCH_3)$.—Diacetylirigenin loses one acetyl easily if heated for a few minutes in alcoholic solution with a little soda. The monacetyl derivative forms no double compound with chloroform, but it dissolves in it readily at the ordinary temperature and may be distinguished in this way from irigenin. From chloroform monacetylirigenin separates in fine, white needles melting at 169°.

Analysis.—Calculated for $C_{20}H_{18}O_9$.

	Per cent. C.	Per cent. H.
Calculated	59.70	4.48
Found	59.75	4.74

Decomposition of Irigenin.—By heating with concentrated alkalies irigenin is decomposed according to the equation

$$C_{18}H_{16}O_8 + 3H_2O = CH_2O_2 + C_{10}H_{12}O_5 + C_7H_8O_4$$

into formic acid, CH_2O_2, an aromatic oxy-acid, $C_{10}H_{12}O_5$, which we call iridinic acid and a phenol which we call iretol.

An alkaline irigenin solution is decomposed differently in presence of oxygen. The decomposition must take place, therefore, with exclusion of air. It is best effected as follows: Fifteen grams irigenin and thirty cc. water are placed in a 500 cc. pressure flask. The air is displaced by hydrogen, ninety grams of a solution of caustic potash (sp. gr. 1.33) corresponding to about thirty grams KOH added, the flask closed as quickly as possible and heated on the water bath for five to six hours. After opening the flask it is acidified at once with thirty grams sulphuric acid which has been diluted with twice the bulk of water. In a well-conducted operation no precipitate will separate from the light yellow acid solution. The formic acid may be distilled off quantitatively in a stream of water vapor; about three hours are necessary. If it is not desired to determine the formic acid, the acid solution is shaken ten to twelve times with ether. The watery residue from the evaporation of the ether is freed from formic acid by distillation in water vapor.

The air in the retort is now replaced by a stream of hydrogen and a boiling saturated solution of barium hydroxide added until the contents are alkaline. The stream of hydrogen is then exchanged for one of carbon dioxide, which precipitates the excess of barium hydroxide. The filtrate from barium carbonate is exhausted with ether. In this way the greater part of the barium iridinate separates in crystals, while the ether takes up the iretol. This is left by distilling off the ether as a syrup, which after some time sets to a mass of crystals. The iridinic acid is obtained by decomposing the barium salt with sulphuric acid and evaporating the filtrate from the barium sulphate.

We have measured the formic acid produced in this reaction. In doing this we have not forgotten that by the prolonged action of hot alkali upon iridinic acid and iretol small amounts of other volatile organic acids are formed as by products. We have determined by comparison with pure iridinic acid and iretol how far the yield of formic acid is affected, and corrected the results obtained in accordance therewith. According to the above equation 100 parts irigenin should give 13.06 per cent. formic acid, 58.9 per cent. iridinic acid, and 43.3 per cent. iretol. We have obtained from 100 parts irigenin as a mean of many determinations: 10.23 per cent. formic acid, forty to forty-five per cent. iridinic acid, and thirty-three to thirty-five per cent. iretol.

In view of the ease with which the product of this reaction decomposes and the fact that secondary decompositions even with careful working cannot be entirely avoided we may conclude with safety from the above figures that the decomposition of iridin as expressed by the above equation corresponds to the facts.

Formic acid, CH_2O.—The formic acid split off from irigenin is identified by its reducing action upon salts of mercury and silver. We have also converted it into ethyl formate as well as into a sodium salt. The latter when analyzed gave:

	Per cent. Na.
Calculated	33.83
Found	33.94

Iridinic acid, $C_{10}H_{12}O_5$.—Iridinic acid is easily purified by recrystallizing from boiling benzene. It forms colorless prisms

melting at 118°, dissolves in water, alcohol, ether, chloroform, acetone and boiling benzene, is less easily dissolved by cold benzene, and is insoluble in light petroleum.

ANALYSIS.

	Calculated for $C_{10}H_{12}O_6$.	Found	
C	56.60	56.45	56.56
H	5.66	5.87	5.85

Heated above its melting point it splits up into carbon dioxide and a phenol which we call iridol.

Iridinic acid is a strong acid. It expels carbonic acid from the carbonates of the metals of the alkalies and alkaline earths and saturates the alkaline hydroxides molecule for molecule. Titration with caustic soda gave the following results:

	For formation of $C_9H_{11}O_5CO_2Na$ is requisite.
Calculated	9.83 per cent. Na
Found	9.80 per cent. Na

The alkaline salts and the calcium salt of iridinic acid are deliquescent. The barium salt, however, crystallizes well. Its composition corresponds to the formula $Ba(C_{10}H_{11}O_5)_2 + 5H_2O$. The water of crystallization is lost at 105°.

ANALYSIS.

	Per cent. H_2O
Calculated for $5H_2O$	13.87
Found	13.90

A barium determination in the dried salt gave:

	Per cent. Ba.
Calculated for $Ba(C_{10}H_{11}O_5)_2$	24.51
Found	24.58

The esters of iridinic acid are formed by passing hydrochloric acid gas through solutions of iridinic acid in the different alcohols.

Methyl iridinate, $C_9H_{11}O_5(CO_2CH_3)$ is a viscous oil, boiling above 360°.

ANALYSIS.

	Calculated for $C_{11}H_{14}O$.	Found.
C	58.41	58.16
H	6.19	6.30

Ethyl iridinate, $C_9H_{11}O_3(CO_2C_2H_5)$ forms a yellow oil which cannot be distilled without decomposition at the ordinary atmospheric pressure.

ANALYSIS.

	Calculated for $C_{12}H_{16}O_8$.	Found.
C	60.00	59.74
H	6.67	6.52

Besides the hydroxyl of the carboxyl group iridinic acid contains a second hydroxyl, whose hydrogen is easily replaced by acyls and alkyls.

Benzoyl iridinic acid, $C_9H_{10}O_2(OCOC_6H_5)(CO_2H)$ is obtained by shaking an alkaline solution of iridinic acid with benzoyl chloride. The substance is precipitated from the alkaline solution by means of hydrochloric acid and recrystallized from alcohol. Its melting point is 131°.

ANALYSIS.

	Calculated for $C_{17}H_{16}O_8$.	Found.
C	64.56	64.58
H	5.07	5.24

Acetyliridinic acid, $C_9H_{10}O_2(OCOCH_3)(CO_2H)$ is formed by heating iridinic acid with acetyl chloride. The excess of acetyl chloride is driven off on the water bath, the residue dissolved in benzene and precipitated with light petroleum. This compound is easily soluble in water, alcohol, ether, benzene, and chloroform, and insoluble in light petroleum, and melts at 125°. Alkalies separate from it acetic acid with great ease. As a control of the composition we have effected this saponification and determined by titration the acetic acid resulting from distillation with sulphuric acid.

100 parts $C_{12}H_{14}O_6$ should give 23.62 parts $C_2H_4O_2$
100 " " have given 24.21 " "

Methyliridinic acid, $C_9H_{10}O_2(OCH_3)(CO_2H)$ crystallizes in white plates easily soluble in water, alcohol, ether, and benzene, insoluble in light petroleum, and melts at 120°. To prepare it iridinic acid is digested in methyl alcohol solution with sodium methylate and methyl iodide. Under these conditions the methyl ester of methyliridinic acid is formed, which by evapo-

ration of the methyl alcohol separates as an oil and is converted by saponification with alkali into methyliridinic acid.

ANALYSIS.

	Calculated for $C_{11}H_{14}O_5$.	Found.
C	58.41	58.22
H	6.15	6.15

Silver Methyliridinate, $C_9H_{10}O_2(OCH_3)CO_2Ag$ is precipitated from the solution of the ammonium salt as a gelatinous mass and obtained by recrystallization from alcohol in beautiful white needles.

Action of Hydriodic Acid upon Iridinic Acid.—By boiling with hydriodic acid, methyl iodide is formed from iridinic acid from which it is evident that it contains methoxyl. We have applied Zeisl's method of methoxyl determination to iridinic acid and obtained the following results:

	Per cent. OCH_3.
Calculated for $2(OCH_3)$ in $C_{10}H_{12}O_5$	29.25
Found	33.13

Iridinic acid therefore contains two methoxyl groups and its formula in accordance with the experiments so far described may be written $C_7H_4(OCH_3)_2(OH)(CO_2H)$.

Iridol, $C_9H_{12}O_3 = C_7H_5(OCH_3)_2(OH)$.—The phenol derived from iridinic acid by splitting off carbon dioxide must have the same formula as that just obtained for the acid. Iridol is obtained by dry distillation of iridinic acid. At 239° a colorless oil passes over which solidifies in the receiver to large white crystals melting at 57°. Iridol is nearly insoluble in cold water, but is easily dissolved by alcohol, ether, ethyl acetate, benzene, chloroform, and caustic alkali. Ferric chloride colors the alcoholic solution violet.

ANALYSIS.

	Calculated for $C_9H_{12}O_3$.	Found	
Per cent. C	64.22	63.81	63.88
Per cent. H	7.14	6.98	7.05

Iridol is a true phenol and is converted on heating with chloroform and caustic alkali into two isomeric aldehydes. One, which belongs to the ortho series, is colored a deep yellow by caustic alkalies like salicylic aldehyde. The second, which is a

derivative of paroxybenzaldehyde does not give this reaction. It crystallizes in white needles which melt at 88°.

Benzoyliridol, $C_7H_5(OCH_3)_2OCOC_6H_5$, is obtained by shaking an alkaline solution of iridol with benzoyl chloride. It dissolves easily in alcohol, ether, and chloroform, as well as in ethyl acetate and crystallizes in white plates which melt at 68°.

ANALYSIS.

	Calculated for $C_{16}H_{16}O_4$.	Found.
Per cent. C.....	70.59	70.31
" H.....	5.88	5.94

Methyliridol, $C_7H_5(OCH_3)_3$, is obtained by the action of methyl iodide upon a methyl alcohol solution of iridolsodium. It is a colorless oil, boiling at 236°–237°.

ANALYSIS.

	Calculated for $C_{19}H_{14}O_3$.	Found.
Per cent. C.....	65.95	65.62
" H.....	7.69	7.71

By oxidation with potassium permanganate methyliridol is converted into *trimethylgallic acid*, $C_6H_2CO_2H(OCH_3)_3$, 3.4.5, which melts at 168°.

ANALYSIS.

	Calculated for $C_{10}H_{12}O_5$	Found.
Per cent. C.....	56.60	56.49
" H.....	5.66	5.78

In order to identify the trimethylgallic acid sharply, we have converted it into gallic acid on the one hand by digestion with hydriodic acid, and on the other hand we have prepared it by methylating gallic acid. Finally we have determined that by dry distillation silver trimethylgallate gives the trimethyl ether of pyrogallol, melting at 47° and boiling at 235°, and that this is converted into pyrogallol when it is heated to 150°–160° in closed tubes with dilute hydrochloric acid.

Trimethylgallic acid and the trimethyl ether of pyrogallol have been known for a long time. W. Will[1] prepared them by permethylating gallic acid and pyrogallol, and G. Körner[2] has shown that the syringic acid obtained by him from the gluco-

[1] *Ber. d. chem. Ges.*, 21, 607 and 2023.

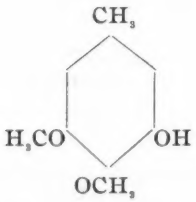
[2] *Gazz. Chim. Ital.*, 18, 216.

side of the elder (dimethylgallic acid) is converted by methylating into trimethylgallic acid of melting point 168°. We have found the properties of the compound in question to be exactly those which W. Will gives it.

Constitution of Iridol.—Trimethylgallic acid is formed from methyliridol by the oxidation to carbonyl of a methyl group attached to the benzene nucleus. Methyliridol corresponds therefore to the formula,

$$C_6H_2(\overset{1}{C}H_3)(\overset{3.4.5}{O}CH_3)_3;$$

it is the trimethyl ether of homopyrogallol, $C_6H_2(\overset{1}{C}H_3)(\overset{3.4.5}{O}H)_3$. Iridol contains one hydroxyl in place of one of the three methoxyl groups of methyliridol. We have already observed that iridol is transformed by chloroform and alkali into two isomeric aldehydes. It must therefore contain two hydrogen atoms in the benzene nucleus, of which one occupies the ortho, the other the para position with reference to the phenol hydroxyl. Only the formula



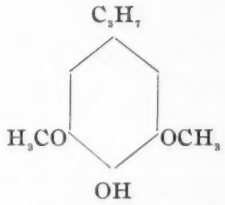
is in accordance with these facts.

There are other grounds for this view. A. W. Hofmann has isolated two phenols from the acid constituents of wood tar boiling between 250°–290°, of which one, boiling at 265°, is a dimethyl ether of homopyrogallol[1] while the phenol boiling at 285° bears the same relation to propylpyrogallol[2]. If we exchange the methyl in the methoxyl groups of these phenols for hydrogen we obtain triatomic phenols which show the characteristic reactions of pyrogallol. For this reason A. W. Hofmann considered these phenols derivatives of pyrogallol.

[1] *Ber. d. chem. Ges.*, **12**, 1371.

[2] *Ber. d. chem. Ges.*, **8**, 67; **11**, 327.

Nitric acid converts the dimethyl ether of propylpyrogallol into the dimethyloxylated quinone[1], $C_6H_2O_2(OCH_3)_2$, melting at 249°. In the first named compound the propyl and hydroxyl groups must occupy the para position with reference to each other. W. Will[2] has shown that the trimethyl ether of Hofmann's propylpyrogallol is converted by potassium permanganate into trimethylgallic acid melting at 168°. The above dimethyl ether of propylpyrogallol must therefore have the formula



It is *a priori* probable that the lower homologue of the above phenols—the dimethyl ether of homopyrogallol—has an analogous constitution. We have, in fact, determined that the neutral methyl ether of the phenol boiling at 265°, prepared by A. W. Hofmann, of which a large sample was at our disposal, had the same properties and the same constitution as the trimethyl ether of homopyrogallol prepared from iridol. Both compounds are converted by the aboxydation of the methyl group attached to the nucleus into trimethylgallic acid melting at 168°.

The dimethyl ether of pyrogallol from the wood tar and iridol are isomeric methyl derivatives of the same homopyrogallol. The properties of the two isomers differ materially as the following summary shows:

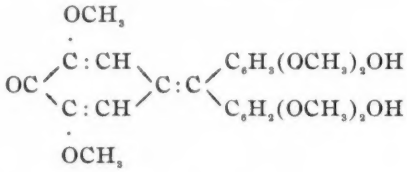
	Dimethyl ether of homopyrogallol from wood tar.	Iridol.
Melts at	36°	57°
Boils at	265°	239°
Benzoyl derivative melts at	118°	68°

By means of a very remarkable method which is analogous

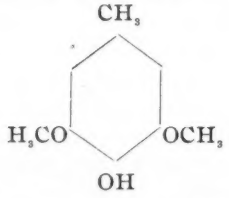
[1] A. W. Hofmann. *Ber. d. chem. Ges.*, 11, 332.

[2] *Ber. d. chem. Ges.*, 21, 2025.

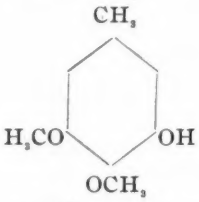
to the formation of rosanilin by the oxidation of a mixture of toluidin and analin, namely, fusion with sodium hydroxide in contact with air, the mixture of the dimethyl ether of homopyrogallol boiling at 265° and of the dimethyl ether of pyrogallol is converted as A. W. Hofmann has shown[1] into eupittonic acid, $C_{20}H_{26}O_9$, the constitution of which, in view of the studies made in the last few years of the triphenylmethane colors should be expressed by the symbol:



To such a condensation, however, only a dimethyl ether of homopyrogallol constituted according to the formula



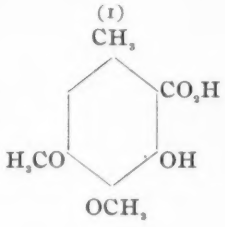
can lend itself. Its isomer, iridol, which under like conditions gives no trace of eupittonic acid or an isomeric eupittonic acid must therefore have the formula,

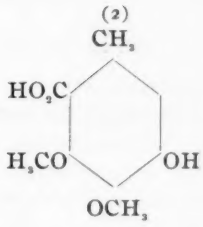


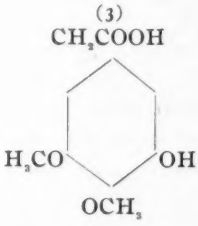
This gives to iridol the same constitution as our experiments.

[1] *Ber. d. chem. Ges.*, 12, 1377.

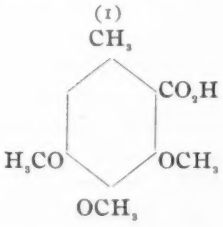
Constitution of Iridinic Acid and Methyliridinic Acid.—Iridinic acid is carboxylated iridol and its composition must correspond to one of the three formulas

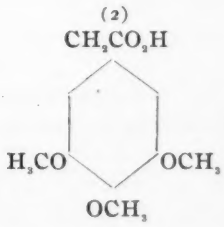






while the constitution of methyliridinic acid is expressed by one of the two formulas





The experiments described below give the further explanation of the constitution of iridinic and methyliridinic acids.

(*a*) *Dibrommethyliridinic Acid*, $C_6\overset{2.6}{Br}_2(\overset{3.4.5}{OCH}_3)_3(\overset{1}{C}H_2CO_2H)$.—If a solution of methyliridinic acid in dilute acetic acid is poured into an excess of bromine water an acid separates in compact crystals which is easily soluble in alcohol and ether. It melts

at 152° and is formed from methyliridinic acid by the substitution of two bromine for two hydrogen atoms.

ANALYSIS.

	Calculated for $C_{11}H_{12}Br_2O_5$	Found.
Per cent. Br	41.66	41.36

The formation of this acid shows at once that of the two formulas considered for methyliridinic acid the second is correct.

(*b*) *Dibromtrimethylgallic Acid.*—Dibrommethyliridinic acid is a very stable compound which may be recrystallized from hot dilute nitric acid without change. If it is heated with nitric acid of sp. gr. 1.2, action takes place accompanied by the evolution of red vapors and soon leads to a profound decomposition of the dimethyliridinic acid used. If, however, the action is stopped at the proper time by the addition of water, which can be determined by the precipitation of crystals instead of an oil, and the solid compound separating dissolved in very dilute nitric acid, dibromtrimethylgallic acid will crystallize out in long lustrous needles which when pure melt at 143°. For comparison we have prepared dibromtrimethylgallic acid by pouring a solution of trimethylgallic acid in dilute acetic acid into excess of bromine water, and find the acid obtained in these different ways to be identical.

ANALYSIS.

	Calculated for $C_{10}H_{10}Br_2O_5$	Found.
Per cent. Br	43.24	43.54

Experiment shows that methyliridinic acid contains two hydrogen atoms directly attached to the benzene nucleus. We have not been able to convert dibrommethyliridinic acid into dibrommethylgallic acid by heating it with potassium permanganate. The potassium permanganate is indeed reduced by heating for a long time and a small part of the dibrommethyliridinic acid destroyed; but by far the larger part of the acid remains unattacked.

(*c*) *Trimethylgallic Acid from Methyliridinic Acid.*—Methyliridinic acid is, on the contrary, readily oxidized to trimethylgallic acid, melting at 168°, by means of potassium permanga-

nate. In carefully conducted oxidations in the course of the transformation an extremely unstable intermediate product, which is difficult to isolate and which is probably the ketonic acid derived from methyliridinic acid, $C_6H_2(OCH_3)_3COCO_2H$, and which we have not followed further.

(*To be continued.*)

ON CARBORUNDUM.

(CARBIDE OF SILICON.)

By Dr. Otto Mühlhaeuser.

THIS new material stands next to diamond, not only in its composition, but in its internal and external properties, in the extraordinary brilliancy of its crystals, and in the extreme hardness which makes it such an efficient and powerful abrasive material.

It is an American invention, having been discovered by Edward G. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles.

The product is obtained by heating a mixture of 100 parts sand, twenty-five parts salt and twenty-five parts coke in an electrical furnace for several hours. The alternating current used has finally a strength of about 500 amperes and a difference of potential of fifty volts.

The mixture yields a mass in which we can distinguish shells and layers of different character and nature. Around the carbon core we find a layer of graphite. The latter is surrounded by a thick shell of carborundum crystals. This shell of carborundum is enveloped in a thin sheet of amorphous carbide of silicon; surrounding and incasing these three products of the reaction is the original mixture in an essentially unchanged condition.

(1) *The Graphite.*—The graphite is located around the carbon core and is covered by the carborundum crystals. It is connected with the latter, forming one large elypsoid of crystals whose rays are arranged radially to the axis of the elypsoid or

core. The inner part of this shell contains the black graphite crystals, the outer the carborundum.

Those parts next to the core consist of pure carbon, and possess all of the properties of graphite—blackening the fingers with metallic luster, feels soft, unctuous, etc. These graphite crystals occur in hexagonal flakes and resemble, sometimes, iodine crystals. Their form is that of the carborundum, out of which they are produced. As wood after being charred still keeps its structure, so carbide of silcon keeps its form when transformed by heat into graphite. The silicon is simply eliminated, $SiC = C + Si$, and a skeleton of the original structure is preserved in carbon.

(2) *The Carborundum Crystals.*—The carborundum crystals occur as the chief products of the reaction between carbon and silicon. They are located between the graphite and a layer of what seems to be an amorphous form of carbide of silicon. The whole mass of the crystals forms a green shell which is easily crushed and separated into the individual crystals. Their color is greenish gray, greenish yellow, greenish blue, etc. Their size differs very much, and depends upon the quantity of material brought into action, on the operation itself, and on the time of the reaction. The crystals are often so small that their shape can only be recognized with the microscope; often so large that they have a diameter of several millimeters.

We must assume that the process takes place according to the equation, $SiO_2 + 3C = 2CO + CSi$; or,

$$(1)\quad 2SiO_2 + 4C = 4CO + 2Si$$
$$(2)\quad 2Si + 2C = 2SiC$$

These crude crystals consist essentially of carbide of silicon, besides some impurities—oxide of aluminum, iron, etc. In order to clean the crystals, to free them from the impurities attached to them, a sample of the crude material as it came from the furnace was crushed, pulverized, floated, and finally prepared in the form of a very fine powder. This was placed in a combustion tube, heated to a red heat, and treated with a current of oxygen. Being thus burnt in oxygen, it was boiled alternately with caustic soda, water, hydrochloric acid, and afterwards it was given a prolonged treatment with hydrofluoric

acid to which a little sulphuric acid had been added. This action being over, all silicon tetrafluoride, hydrofluoric and sulphuric acids were driven off, and the powder washed and dried.

By this treatment carbide of silicon was obtained in an almost pure state.

The pure silicon carbide has a specific gravity of 3.22. It is insoluble in all of the ordinary solvents, as hydrochloric, nitric, sulphuric, and hydrofluoric acids, but it is decomposed by caustic and carbonated alkalies.

Heated to a white heat in a platinum crucible, the powder shows a yellow green golden color of remarkable beauty, some of the powder being at the same time burnt up. The loss per hour is about one-half per cent. This indicates that silicon carbide is very little combustible in oxygen:

$$CSi + 4O = CO_2 + SiO_2.$$

It is easy to decompose it by heating with substances like chromate of lead or oxide of iron, and with a mixture of chromate of lead and bichromate of potash it even explodes.

The very fine powder, when floated in water, does not entirely settle, even after several months; this property of suspension is, however, immediately ended by adding acids or salts.

(3) *The Amorphous Carbide of Silicon.*—This substance forms a layer of greenish gray, bluish green, and white particles of the size of the original sand from which they evidently originate. The particles have no definite form, are very soft and therefore easily crushed to a fine powder, and this was found to contain the same constituents as the carborundum. It was evident that it was an amorphous form of carbide of silicon and therefore a somewhat similar process of purification was employed.

The cleaned powder consists essentially of silicon carbide in an amorphous form. Its specific gravity is 3.22, the same as the crystallized variety. It seems, however, to be more easily combustible.

(4) *The Unaltered Mass.*—The next material we come to is a mass of the original mixture, which has been very little, or not at all, changed by the operation of the furnace.

(5) *The Gases.*—The gases evolved at the beginning, during, and near the ending of the reaction have been analyzed. They consisted of a mixture of hydrocarbons derived from fresh coke and oxide of carbon with a small admixture of air.

Samples are not shown because you probably have already seen the display of this splendid material in the gallery of the mining building. This new material seems to me likely to cause a revolution in the abrasive market.

RAPID METHOD FOR THE DETERMINATION OF MANGANESE IN MANGANESE BRONZE.

By Jesse Jones.

Received September 21, 1893.

THE following method is in use in this laboratory for the determination of manganese in manganese bronze. It is an adaptation of a well-known method in common use for the determination of manganese in iron and steel. A determination can be made in less than one hour, and as the amount of manganese in the ordinary run of work seldom exceeds 0.10 per cent., the method gives fairly satisfactory results.

The Method.—Dissolve five to ten grams of drillings in nitric acid of 1.20 sp. gr., using a large beaker to avoid frothing over. An excess of acid must be avoided as it interferes with the precipitation of the copper by hydrogen sulphide. When solution is complete, transfer to a 500 cc. cylinder without filtering out the precipitated stannic oxide. Make up to 300 cc. and pass a rapid current of hydrogen sulphide from a Kipp's apparatus until the supernatant liquid is colorless. Decant off through a dry filter, 180 cc. corresponding to three or six grams of sample, and boil down rapidly to about ten cc. Transfer to a small beaker and add twenty-five cc. of strong nitric acid. Boil down one-half, make up with strong nitric acid, boil, and add one spoon full of potassium chlorate. Boil ten minutes and add another spoon full of potassium chlorate. Boil till free from chlorine, cool in water, and filter on asbestos, using filter pump. Wash with strong nitric acid through which a stream of air has been passed. When free from iron wash with cold water until no acid

remains. Place the felt and precipitate in the same beaker and dissolve in ferrous sulphate, using five cc. at a time. Titrate back with permanganate until a pink color remains. Deduct the number of cc. used in titrating back, from the number of equivalents of ferrous sulphate used and the remainder shows the manganese in the amount of sample taken.

Permanganate Solution.—Dissolve 1.149 grams potassium permanganate in 1,000 cc. water; one cc. equals one mgm. manganese. Check by dissolving 0.1425 grams ferrous-ammonium sulphate in a little water and acidulating with hydrochloric acid. This should precipitate ten mgms. of manganese. If not, apply the factor of correction.

Ferrous Sulphate Solution.—A solution of ferrous sulphate in two per cent. sulphuric acid, so dilute that five cc. corresponds to ten cc. permanganate solution. This is best made by trial and dilution.

CHEMICAL LABORATORY,
WM. CRAMP & SONS, PHILADELPHIA.

PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

Ore Separators, etc.—**501,022,** July 4, McCoy, J. H., ore concentrator. **500,662,** July 4, Lockhart, W. S., ore separator. **500,604-605-606,** July 4, Payne, C. Q., magnetic ore separator. **501,879,** July 18, Fitzgerell, J. J., ore separator and amalgamator. **501,999,** July 25, Fraser, A., ore crushing machine. **501,494,** July 18, Davis, O. W., Jr., ore roasting kiln. **500,582,** July 4, Jones, J. M., ore pulverizer. **501,188,** July 11, Iles, M. W., flooring for blast furnaces. **500,621,** July 4, Sheedy, D., and M. W. Iles, apparatus for separating matte from slag. **502,167,** July 25, Bates, F. G., metallurgical furnace. **500,684,** July 4, Westerman, F., regenerative coke oven. **501,107,** July 11, Siemens, F., regenerative gas furnace and producer. **502,181,** July 25, Fauvel, C. J., refractory ores, treatment of; incandescent particles of freshly roasted ores are struck as they descend by crossing jets of water, while the air is excluded. **501,996,** July 25, Emmens, S. H., electrolytic bath. **501,997,** July 25, Emmens, S. H., electrolytic separation of metals. **501,783,** July 18, Hermite, E., electrolysis of saline solutions, using a thin layer of mercury to form amalgam of metal with base.

Iron and Steel.—**501,200,** July 11, Wailes, J. W., open-hearth steel melting furnace. **501,138-139-140,** July 11, Heath, J., and Holden, G. H., apparatus for manufacture of iron and steel. **500,979,** July 4, Tweedy, E., apparatus for hardening steel.

Lead.—**501,377,** July 11, Smith, A. J., white lead; charge is put in corroding chambers with acid vapors and basic cream of varying degrees of concentration. **500,580,** July 4, Iles, M. W., flue dust from lead smelting furnaces is charged into fusion furnaces; fused quickly; fumes are collected in screens and fusions are run out and allowed to cool.

Zinc.—**501,189,** July 11, Lewis, G. T., alkali is added to sulphide ores and roasted to produce zinc oxide. **501,559,** July 18, Chanute, A., metals from compound ores containing zinc; ores are mixed with salt, roasted, fumes collected in screens, and leached with dilute hydrochloric acid, and gold and silver are separated by adding zinc to solution.

Aluminum.—**501,553,** July 18, Whitney, C. F., alloy, aluminum, 76 per cent. or more, manganese and tungsten, 12 per cent. each or less. **501,233,** July 11, Richards, J. W., and Hunt, A. E., alloy, aluminum, iron and manganese (30 per cent.) with a low per cent. of carbon.

Nitric Acid.—**500,786,** July 4, Volz, C. O., the charge is placed in retort and distilled in vacuo.

Ammonia and Cyanides.—**500,650-651,** July 4, Fogarty, T. B., apparatus for manufacture.

Ammonium Nitrate.—**500,914,** July 4, Landin, J., alcohol is percolated through a solution of sodium nitrate and ammonium sulphate, and the alcoholic solution is passed through ammonium sulphate.

Chlorine, or Caustic Alkali.—**501,121,** July 11, Waite, C. N., electrolytic method, brine being first treated to form insoluble sulphates.

Quinin, etc.—**501,066,** July 11, Grimaux, E., manufacture of halogen derivatives such as chlor-hydro-sulphate. **500,665,** July 4, Marckwald, W., manufacture of piperazin. **501,446,** July 11, Schaal, E., manufacture of resin acid esters.

Tanning, etc.—**501,586,** July 18, Claxton, J. W., tanning hides; composition for, red oak bark, white oak bark, ash bark, salt, lye soap, soda, gum gambria, alum, and sodium phosphate. **501,797,** July 18, Lussigny, H. A. A., carrotting furs; caustic alkali is used. **501,798,** ditto; carbon and nitric acid are employed.

Sugar.—**502,014-015,** July 25, Prangey, L. E. A., process of refining. **501,878,** July 18, Engel, G., ditto.

Distillation of Mash.—**502,079,** July 25, Ilges, R., process of separating fusel oil.

Water.—**501,784,** July 18, Herscher, C., sterilization of drinking water. **501,732,** July 18, Roeske, H., purifying water by adding stratum of iron, which is agitated and subjected to electric current, filtering and aerating the water after treatment. **502,252,** July 25, Hanna, D., purifying water for steam boilers.

Earthenware.—**500,585,** July 4, Klieber, J., liquid material for manufacture—clay and aqueous solution of sodium carbonate or bicarbonate.

Plasters and Cement.—**501,937,** July 25, Hawes, E. E., cement, tar, rosin, glue, vinegar, salt, flour, and sal soda. **501,794, 501,888-889,** July

18, Laffont, M., artificial stone, "plastic refractory argil and fusible calcined argil." **502,023**, July 25, Turner, J. W., artificial stone, Portland cement, rock-lime, plaster of Paris, marble dust, and sand. **502,096, 502,097**, July 25, Heller, T. J., plaster compound, sodium silicate, sodium carbonate, alum, sugar, senegal gum, salt cake, and ground china ware.

Oils and Varnishes.—**501,988**, July 25, Carman, F. J., refining sulphurous petroleum; passing vapors through a mass of melted metal, which will reduce the sulphur and combine with it. **501,227**, July 11, Hojer, T. G., preservative drier, hydrated manganese dioxide, slaked lime, and a lime salt. **501,578**, July 18, Pfaune, H., varnish; made by electrolyzing linseed oil which has been acidulated with dilute sulphuric acid.

Bleaching and Dyeing.—**500,917**, July 4, Lifschütz, I., violet red dye from dinitro-anthraquinone. **501,500**, July 18, Gano, Leo, bluish black tetrazo compound of paradiamines. **501,118**, July 11, Ulrich, M., and Lauch, R., blue black tetrazo. **501,434**, July 11, Müller, C., violet, sulphuretted derivative of ortho-alkyl-oxy-para-rosaniline. **501,104**, July 11, Runkel, F., greenish blue triphenylmethane dye. **501,069**, July 11, Hassencamp, H., violet triphenylmethane dye. **500,761-762**, July 4, Green, A. G., and Lawson, T. A., red azo dyes. **500,558**, July 4, Bracewell, John, printing anilin black. **501,156**, July 11, Ostersetzer, O., printing cotton fabrics. **501,160**, July 11, Fitzinger, W., dyeing black.

Oxygen from Air.—**500,697**, July 4, Webb, G., Jr., composition for; made by dissolving caustic soda in hot water, heating to 100° C., adding manganese oxide and sodium manganate, evaporating to dryness, heating, cooling and breaking.

Miscellaneous.—**500,549**, July 4, Baekeland, L. H., antiseptic compound; contains sodium and potassium fluoride and common salt. **501,471**, July 11, Shaw, C. H., sulphur candle, **501,036**, July 4, Allen, D., soft soap ingredients; hard soap, sodium carbonate, phosphate, and chlorate, concentrated lye and water. **500,934**, July 4, Nirdlinger, M., artificial fuel; bituminous coal, anthracite coal, silicate of soda, dilute sulphuric acid, coal tar and coal tar pitch, manganese dioxide, and potassium chlorate. **501,323**, July 11, Bryant, W. E., insecticide, for stored grain; sulphur, slaked lime, sodium sulphite, potassium nitrate, sassafras bark, gum, camphor, and thymol. **501,235**, July 11, Seifert, B. R., creosote composition; derivative from creosote and carbon dioxide. **501,845**, July 18, Pohle, J. G., stove polish; plumbago, phosphoric acid and a hygrometric substance. **501,254**, July 11, Pohle, J. G., stove polish; plumbago and phosphoric acid. **502,163**, July 25, Apple, C. S., adhesive pencil; dextrin, cold water, glue, zinc white and glucose are used. **501,222**, July 11, Dame, Paul C., artificial whale bone, made from animal hair; put first in softening bath, then in a bath of acetic acid, and then pressure is employed. **501,311-312**, July 11, Albertson, and Briggs, N. B., coloring and burnishing compound; soap, wax, shellac, borax, dextrin, glue, water, coloring matter, and chromic acid are used.

NEW BOOKS.

A Laboratory Manual, Containing Directions for a Course of Experiments in Organic Chemistry. Systematically Arranged to Accompany Remsen's Organic Chemistry. By W. R. Orndorff, A. B., Ph.D., Assistant Professor of Chemistry in Cornell University. D. C. Heath & Co. 12mo.

This book, printed on one side of the paper only, to leave room for notes evidently, contains directions for eighty-two experiments, beginning with "Fractional Distillation" and ending with "Alizarin." The apparatus used is as simple as the nature of the work will allow and the questions asked or indicated by means of an interrogation mark seem to be judicious. The directions bear evidence of having been tried carefully in practice. The absolute necessity for this would seem to be self-evident, but I venture to say that in very many books of the kind it has nevertheless not been done—so much the worse for the unlucky student who repeatedly endeavors to do the impossible because his authority is good. It cannot be too strongly insisted upon that such books ought either to be put together conscientiously or not at all. E. H.

The Pharmacopœia of the United States of America. Seventh Decennial Revision (1890). Official from January 1, 1894. Published by the Committee of Revision. Philadelphia: J. B. Lippincott Company. Agents, P. Blakiston, Son & Co. 1893.

The Pharmacopœia of the United States has become a book of considerable dimensions—602 pages.

The metric system has been employed throughout the volume, the solids by weight and the liquids by measure. Of the coal tar antipyretics, acetanilid is the only one admitted, because the others are either made by a patented process or their names have a proprietary right. Among the articles added to the Pharmacopœia I notice peroxide of hydrogen, convallaria, cocaine, hyoscine, sparteine, strontium bromide, and pepsin (1 : 3000). The terminal "e" is retained for chlorine, cocaine, bromide, *et altera*. Instead of writing chloride of sodium, or nitrate of silver, the committee make it sodium chloride, silver nitrate, and so on, putting the base first. In the case of the salts of iron and mercury this change involved the use of the respective

terms in "ous," and "ic" (ferrous and ferric, mercurous, mercuric); but as a matter of precaution they have retained "corrosive," "mild," "yellow," and "red" in the title of the respective mercury compounds; thus, "corrosive mercuric chloride," "mild mercurous chloride." Instead of the word, "officinal," "official" is now used.

The present Pharmacopœia contains 994 articles, ninety of those previously official having been dropped, while eighty-eight new ones have been introduced. Commercial ether and commercial chloroform have been dismissed. Arsenium becomes arsenum; aluminium becomes aluminum; creasotum is now creosotum. The work throughout is gotten up with good taste, well printed on good paper. The accuracy of the work is guaranteed by the high standing of the committee of revision.

ISAAC OTT.

NOTES.

Immunity Against Disease.—The following appears on the editorial page of the *American Druggist* for October 12, under the caption "Germ Nuclein," and as it contains matter of general interest to chemists it is reprinted here entire.

Recent investigations of Dr. Victor C. Vaughan, of the University of Michigan, into the principles of immunity and cure in the infectious diseases, as illustrated in his presidential address to the Section on General Medicine of the Pan-American Medical Congress, mark so remarkable a step in the progress of modern bacteriology as to compel most willing admiration for the man and his work. The artificial production of immunity from disease dates back to 1796 when Jenner first made known his discovery with reference to the prevention of smallpox by inoculations of a mild form of the infection. Since then the subject of immunity against disease has received most careful consideration from many of the most brilliant thinkers in the scientific world, until it is now regarded as a special subject of scientific study, while at the same time finding place in the schools of medicine as one of the special branches of study in that science. Pasteur, the eminent French chemist, has particularly distinguished himself in this field, and his labors have won for him with other honors that of election to membership in the French Academy. His success in the treatment of rabies by inoculating the patient with sterilized cultures of the pathogenic germ, has made his name known in all parts of the civilized world, though scieutists are not yet prepared to

admit that the treatment is either entirely curative or preventative. With regard to Pasteur's success in the prevention of chicken cholera and anthrax by the introduction into the tissues of modified forms of the specific germs of these diseases, it should be known that his teachings on the subject are accepted as authoritative in all schools of bacteriology.

Immunity against disease may be either artificial or acquired; and the induction of artificial immunity, according to Vaughan, may be brought about either by an attack of the disease ending in recovery; by direct inoculation with the germs of disease, according to certain recognized methods providing for either (1) vaccination with a modified or less virulent form of the infection; or (2) the introduction of at first a very small number of the virulent germs and successive inoculations with larger numbers; or by one or more treatments with sterilized cultures of the germs.

In studying the production of immunity from infectious diseases by the method of treatment with sterilized cultures, the question naturally presented itself to Dr. Vaughan as to what constituent of the culture conferred immunity, and it is from the study of this question that he has built up his theory regarding the rôle of the germ-nuclein. He has gone over the ground traversed by a number of German investigators, and, to quote his own words, he is "ready to believe that the immunizing substance is a constituent of the bacterial cell itself;" and is, besides, a poison which is capable of acting as an antidote to the greater poison of infection when administered in small doses with the latter purpose in view.

Dr. Vaughan has not limited his investigations to this either, but has proceeded further and succeeded after much experimentation in isolating active nucleins from various cellular bodies. The preparation, chemical reaction, germicidal properties and physiologic effect of these nucleins are described in detail in his address to the Pan-American Medical Congress which is printed in part in the October 7 number of that excellent medical journal, the Philadelphia *Medical News*.

The new field of study opened up by Dr. Vaughan will doubtless be fruitful of research not less in the domain of chemistry than of medicine, though practical applications of the study in its bacteriological aspect may not ensue for some years to come. Many persons who read for the first time of Dr. Vaughan's researches into the germicidal properties of the nucleins obtained from glandular organs like the testicles, thymus and thyroid will find a corroboration of the claims made in very recent times as to the therapeutic value of certain organic extracts, but further study will convince all such that the germ-nuclein theory is founded upon a more scientific basis and bears no more relation to the former than does the medication of the present day with that of ancient times.